Società Chimica Italiana

Atti del XXVI Congresso Nazionale della Società Chimica Italiana

Centro Congressi Hotel Ariston
Paestum (SA), 10-14 settembre 2017

Volume V

- Divisione di Chimica Industriale
- Divisione di Chimica Inorganica
- Divisione di Chimica dei Sistemi Biologici
- Divisione di Spettrometria di Massa

Società Chimica Italiana
Roma, Italia
www.soc.chim.it

ISBN 9788886208802
ISBN 9788886208857

SPONSOR ISTITUZIONALI
Università degli Studi di Salerno

Dipartimento di Farmacia

Dipartimento di Chimica e Biologia A. Zambelli

GOLD SPONSOR

BRONZE SPONSOR

SUPPORTERS

Patrocinio

Sommario

DIVISIONE DI CHIMICA INDUSTRIALE

Comitato Scientifico

- Francesco Pignataro, Presidente della Divisione di Chimica Industriale
- Giorgio Strukul, Università degli Studi di Venezia, Ca' Foscari
- Fabrizio Cavani, Università degli Studi di Bologna
- Martino Di Serio, Università degli Studi di Napoli, Federico II
- Michela Signoretto, Università degli Studi di Venezia, Ca' Foscari
- Gaetano Guerra, Università degli Studi di Salerno
- Paolo Pollesel, Eni SpA

Delegato di Divisione

- Vincenzo Venditto, Università degli Studi di Salerno

Programma Scientifico

Divisione di Chimica Industriale

Lunedì 11 Settembre 2017

	Sala Hera
Session I - Catalysis and Green Chemistry	
Chairperson Fabrizio Cavani	
9:00 – 9:20	IND-OR01: Elnaz Bahadori, Matteo Compagnoni, Antonio Tripodi, Laura Prati, Carlo Pirola, Gianguido Ramis, Ilenia Rossetti. *CO_2 photoreduction at high pressure to both gas and liquid products over titanium dioxide: the effect of unconventional reaction conditions.*
9:20 – 9:40	IND-OR02: Giuseppe Bonura, Catia Cannilla, Fabio Costa, Aldo Mezzapica, Francesco Frusteri. *How structural and surface properties affect stability of hybrid CuZnZr-zeolite catalysts during DME synthesis via CO_2 hydrogenation.*
9:40 – 10:00	IND-OR03: Filippo Bossola, Xavier Isidro Pereira-Hernández, Claudio Evangelisti, Yong Wang, Vladimiro Dal Santo. *Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol.*
10:00– 10:20	IND-OR04: Emilia Paone, Rosario Pietropaolo, Francesco Mauriello. *Selective arene production from aromatic ethers promoted by Pd/Fe_3O_4 catalyst under transfer hydrogenolysis conditions.*
10:20 – 10:40	IND-OR05: Riccardo Balzarotti, Matteo Ambrosetti, Gianpiero Groppi, Enrico Tronconi. *Investigation of coating deposition and catalytic activation of Periodic Open Cellular Structures (POCS) by spin-coating.*
10:40 – 11:00	Coffee Break
	Sala Hera
Session II - New Materials	
Chairperson Rinaldo Psaro	
11:00 – 11:20	IND-OR06: Pier Paolo Prosini, Mariasole Di Carli, Livia Della Seta, Maria Carewska, Ivan Fuso Nerini. *Ethylene vinyl acetate: a promising binding material for high power-high energy electrodes with a prolonged cycle life*
11:20 – 11:40	IND-OR08: Vincenzo Villani, Vito Lavallata. *Unexpected viscoelasticity of Polydimethylsiloxane liquid blends.*
	Sala Hera
Flash Presentation Session 12:00-13:00	
Chairperson Martino Di Serio	
	IND-FC01: Francesca Coló, Federico Bella, Jijeesh R. Nair, Claudio Gerbaldi. *Polymer electrolytes prepared by industrially compatible processes for renewable energy storage in sodium batteries.*
	IND-FC02: Antonio De Luca, Emanuele Piciollo, Cluadio Picchi, Alessio Ceccarini, Emanuele Salvietti, Francesco Di Benedetto, Stefano Caporali, Stefano Martinuzzi, Massimo Innocenti. *Thin film of black-gold by electrodeposition, for jewellery making.*
	IND-FC03: Grazia Leonzio. *Study of Fenton reactor in a wastewater treatment plant.*
	IND-FC04: Giada Innocenti, Andrea Malmusi, Matteo Della Pasqua, J. Velasquez Ochoa, Fabrizio Cavani. *Isoprene production from methanol: an investigation on the reaction mechanism.*

	IND-FC05: David Hermann Lamparelli, Antonio Buonerba, Nunzia Galdi, Leone Oliva. *Diblock copolymer ethylene-syndiotactic styrene.*
	IND-FC06: Federica Leone, Andrea Gignone, Silvia Ronchetti, Roberta Cavalli, Luigi Manna, Mauro Banchero, Barbara Onida. *An organic-solvent-free route to obtain nanostructured zinc oxide-based reservoir of clotrimazole.*
	IND-FC07: Marino Malavolti, Antonietta Schirò, Marco Cerra. *Cool Roofing, where chemistry indirectly helps environment.*
	IND-FC08: Mattia Melloni, Fabrizio Cavani, Anna Maria Raspolli Galletti, Hilda Gomez Bernal, Claudia Antonetti. *Integrated catalytic process for biomass hydrolysis: a comparison of different pretreatments and catalysts.*
	IND-FC09: Wanda Navarra, Olga Sacco, Vincenzo Vaiano, Diana Sannino, Christophe Daniel, Vincenzo Venditto. *Removal of non-degradable organic compounds from water with photocatalytic nanocomposite aerogels.*
	IND-FC10: Veronica Pragli, Elnaz Bahadori, Matteo Compagnoni, Gianguido Ramis, Ilenia Rossetti. *Heterogeneous photocatalytic processes for the abatement of N-containing pollutants from wastewater.*
	IND-FC11: Francesco Puzzo, Giulia Pavarelli, Carlo Lucarelli, Fabrizio Cavani. *The upgrading of bio-alcohols: production of added-value chemicals by the gas-phase (oxi)dehydration of 1-butanol over V/P/O catalysts.*
	IND-FC12: Antonietta Cozzolino, Paola Rizzo, Gaetano Guerra. *Antimicrobial release from s-PS Active Packaging.*
	IND-FC13: Antonella Salvini, Arianna Bracciali, Bernardo Grossi, Donatella Giomi, Mario Tredici, Liliana Rodolfi, Massimo D'Ottavio, Luca Meschisi, Alberto Brandi. *Biorefinery from the marine microalga Nannochloropsisoceanica.*
	IND-FC14: Michela Signoretto, Alberto Olivo, Maela Manzoli, Ilenia Rossetti, Mercedes Maroto-Valer. *Lookingat the bigger picture in carbondioxidephotoreduction.*
	IND-FC15: Maria Ricciardi, Raffaele Cucciniello, Daniele Cespi, Carmine Capacchione, Ivano Vassura, Fabrizio Passarini, Antonio Proto. *Synthesis of monoalkylglyceryl ethers using glycidol as green starting material.*
13:00 – 14:00	Intervallo Pranzo – Lunch Break
	Sala Hera
14:00 – 15:00	***Assemblea dei soci del Gruppo Interdivisionale di Catalisi*** ***Riunione Comitato Direttivo Divisione Chimica Industriale***
	Sala Paestum B
14:00 – 15:00	*Poster Session (IND-FC01 – IND-FC15)*
	Sala Hera
	Session III - Homogeneous Catalysis
	Chairperson Antonella Salvini
15:00 – 15:20	IND-OR09: Carlo Bravin, Donato M. Mancino, Giulia Licini, Cristiano Zonta. *Molecular recognition and catalysis within confined space.*
15:20 – 15:40	IND-OR10: Cristiano Bolchi, Francesco Bavo, Marco Pallavicini. *Producing amino acid benzyl esters under ecofriendly conditions and without racemization.*
15:40 – 16:00	IND-OR11: Alberto Villa, Ilenia Rossetti, Laura Prati, Aditya Savara. *Microkinetic modeling of benzyl alcohol oxidation on Pd and AuPd catalysts.*
16:00 – 16:20	IND-OR12: Federica Sabuzi, Pierluca Galloni, Valeria Conte. *Sustainable bromination of thymol: synthesis of new biologically active compounds.*
16:20 – 16:40	IND-OR13: Paolo Centomo, Chiara Dalla Valle, Francesco Frison, Marco Zecca. *New perspectives in the action of halide ions as promoter for the direct synthesis of hydrogen peroxide over palladium catalysts.*

16:40 – 17:00	Coffee Break
	Sala Hera
	Session IV - Catalysis and Materials
	Chairperson Paolo Pollesel
17:00 – 17:20	IND-OR14: Federico Bella, Anders Hagfeldt, Michael Grätzel, Claudio Gerbaldi. *Current efforts to make perovskite solar cells industrially viable*
17:20 – 17:40	IND-OR15: Silvia Bordiga, Elisa Borfecchia, A. Martini, Chiara Negri, Gloria Berlier, Pablo Beato, Kirill A. Lomachenko, Carlo Lamberti, Dimitrios K. Pappas, Michael Martin Dyballa, Stian Svelle, Unni Olsbye. *Composition and temperature dependent Cu-speciation in Cu-SSZ-13 catalysts: an in situ XAS and FTIR study.*
17:40 – 18:00	IND-OR16: Vito Di Noto, Keti Vezzù, Enrico Negro, Federico Bertasi, Giuseppe Pace. *Conductivity and relaxation phenomena in ion conducting materials by broadband electric spectroscopy.*
18:00– 18:20	IND-OR17: Galliano Simone, Bella Federico, Falco Marisa, Barolo Claudia, Giordano Fabrizio, Boschloo Gerrit, Grätzel Michael, Hagfeldt Anders, Gerbaldi Claudio, Viscardi Guido. *Biosourced polymers for aqueous solar cells: a possible breakthrough towards green photovoltaic commercialization.*
18:20 – 18:40	IND-OR18: Olga Sacco, Vincenzo Vaiano, Wanda Navarra, Christophe Daniela, Vincenzo Venditto. *Development of N-doped TiO_2 catalyst for the photocatalytic treatment of wastewater in presence of visible light irradiation*
18:40 – 19:00	IND-PZ01: Parmaliana Award Lecture by Matteo Monai *Nanostructured materials for environmental and energy-related applications*
	Sala Hera
19:00 – 19:30	***Assemblea ordinaria Divisione di Chimica Industriale***
19:30 – 20:00	***Assemblea straordinaria GISAC (Gruppo Interdivisionale Sicurezza in Ambiente Chimico)***

Martedì 12 Settembre 2017

	Sala Hera
	Session V - Catalysis and Polymers
	Chairperson Vincenzo Venditto
9:00 – 9:20	IND-OR19: Maria Michela Dell'Anna, Matilda Mali, Giuseppe Romanazzi, Antonino Rizzuti, Cristina Leonelli, Piero Mastrorilli. *Polymer supported palladium nanoparticles as catalyst for organic reactions in water.*
9:20 – 9:40	IND-OR20: Rosa Vitiello, Rosa Turco, Vincenzo Russo, Martino Di Serio, Riccardo Tesser. *Bromobutyl rubber synthesis: influence of the reaction temperature on product distribution.*
9:40 – 10:00	IND-OR21: Rosita Lapenta, Antonio Buonerba, Assunta De Nisi, Magda Monari, Alfonso Grassi, Stefano Milione, Carmine Capacchione. *Stereorigid OSSO-Type group 4 metal complexes in the polymerization of olefins and polar monomers.*
10:00 – 10:30	IND-IL01: Invited Lecture by Gaetano Iaquaniello *What role will chemistry and chemical engineering play in creating a sustainable and prosperous word*
10:30 – 10:50	Coffee Break
	Sala Hera
	Session VI - Materials and Formulations I
	Chairperson Michela Signoretto

10:50 – 11:20	IND-IL02: Invited Lecture by Amilcare Collina *Materials chemistry for sustainable buildings: a review of MAPEI technologies.*
11:20 – 11:40	IND-OR22: Elena Ghedini, Michela Signoretto, Alessia Costantin, Alessandria Semenzato, Giuseppina Cerrato. *Smart formulations for cosmetic industrial applications.*
11:40 – 12:00	IND-OR23: Matteo Guidotti, Rinaldo Psaro, Elisabetta Gargani, Alessandro Caselli, Enrico L. Appiani, C. Cattaneo, Roberto Rappuoli. *Inorganically and organically modified mineral clays: a sustainable approach in the control of the olive tree fly pest, Bactroceraoleae.*
12:00 – 12:20	IND-OR24: Mirco Nodari, Aldo Longo, Dino Ferri, Andrea Perolo. *Modeling approach for applied research: the case-study of PLA synthesis by ring-opening polymerization of lactide*
12:20 – 12:40	IND-OR25: Massimo Innocenti, Maurizio Passaponti, Emanuele Salvietti, Stefano Martinuzzi, Emanuele Piciollo, Stefano Mariottini, Luca Rosi, Stefano Caporali, Walter Giurlani, Francesco Di Benedetto. *Chemical research in the field of galvanic industries and fashion accessory.*
12:40 – 13:00	IND-OR26: Anna Malafronte, Claudio De Rosa, Finizia Auriemma, Carmen Sasso. *Manipulating the arrangement of arrays of nanoparticles on solid supports by using self-assembled block copolymers templates.*
13:00 – 14:00	Intervallo Pranzo – Lunch Break

Mercoledì 13 Settembre 2017

	Sala Paestum B
14:00 – 15:00	*Poster Session(IND PO01 – IND PO13)*
	Sala Hera
	Sessione VII- MSc and PhD Thesis Awards
	Chairperson Federico Bella
15:00 – 15:10	IND-PZ02: Best MSc Thesis Award, lecture by Massimo Christian D'Alterio. *DFT-D Study of crystal phase transitions in syndiotactic polypropylene*
15:10 – 15:20	IND-PZ03: Best MSc Thesis Award, lecture by Cristina Pizzolitto. *Development of nanostructured nickel based catalysts for hydrogen production*
15:20 – 15:35	IND-PZ04: Best PhD Thesis Award, lecture by Sebastiano Campisi. *Novel approaches towards the optimisation of metal nanoparticle based catalysts*
15:35 – 15:50	IND-PZ05: Best PhD Thesis Award, lecture by Tommaso Tabanelli. *Sustainable catalytic processes for the synthesis and use of organic carbonates*
	Sala Hera
	Session VIII - Materials and Formulations II
	Chairperson Federico Bella
15:50 – 16:10	IND-OR27: Giorgio Ferrari. *New Sustainable Technology to Recover Returned Concrete.*
16:10 – 16:30	IND-OR28: Raffaella Mancuso, Roberta Amuso, Biagio Armentano, Anna R. Cappello, Francesco Galiano, Alberto Figoli, Jan Hoinkisd, Bartolo Gabriele. *Acryloxyalkyltriethylammonium bromides: useful starting materials for the preparation of polymeric membrane coatings with anti-biofouling properties.*
16:30 – 16:50	**Coffee Break**
	Sala Hera
	Session IX- Biochemicals
	Chairperson Francesco Pignataro
16:50 – 17:10	IND-OR29: Paolo Centomo, Chiara Dalla Valle, Federico Rastrelli, Sandro Campestrini, Marco Zecca. *Novel ion-exchange catalysts for the esterification of vegetable oil solutions of fatty acids with methanol*

17:10 – 17:30	IND-OR30: Domenico Licursi, Claudia Antonetti, Sara Fulignati, Alessandro Corsini, Anna Maria Raspolli Galletti. *The hydrothermal conversion of cellulose-rich wastes deriving from the papermaking process to levulinic acid as smart opportunity for their re-use and valorization.*
17:30 – 17:50	IND-OR31: Vincenzo Russo, Rosa Vitiello, Rosa Turco, Riccardo Tesser, Martino Di Serio. *Levulinic acid esterification kinetics with ethanol in the presence of Amberlyst-15.*
17:50 – 18:10	IND-OR32: Nicola Scotti, Federica Zaccheria, Claudio Evangelisti, Rinaldo Psaro, Nicoletta Ravasio. *Dehydrogenative coupling promoted by copper catalysts: a way to upgrade bio-alcohols*
18:10 –18:30	IND-OR33: Rosa Turco, Martino Di Serio, Marcella Mazzocca, Vincenzo Russo, Riccardo Tesser, Rosa Vitiello, Donatella Cimini, Chiara Schiraldi. *Succinic acid Production from ArundoDonaxhydrolysate for bio-based poly(butylene succinate) synthesis.*
18:30 – 18:50	IND-PZ06: Mario Giacomo Levi Award Lecture by Fabrizio Cavani and Mario Novelli *n-Butane to Maleic anhydride: an impossible reaction and a catalyst which does miracles*
18:50 – 19:10	IND-OR34: Ferruccio Trifirò. *The history of the journal "La Chimica e l'Industria"*

Premi
della Divisione di Chimica Industriale

Premio Mario Giacomo Levi

Prof. Fabrizio Cavani, Università degli studi di Bologna

Dott. Ing. Mario Novelli, Polynt SpA

Premio Adolfo Parmaliana

Prof. Matteo Monai, Università degli Studi di Trieste

Premi Tesi di Laurea

Dott. Massimo C. D'Alterio, Università degli Studi di Napoli Federico II

Dott. Cristina Pizzolitto, Università degli Studi di Venezia

Premi Tesi di Dottorato

Dott. Sebastiano Campisi, Università degli Studi di Milano

Dott. Tommaso Tabanelli, C.I.R.I.-E.A.

Nanostructured materials for environmental and energy-related applications Premio Adolfo Parmaliana

Matteo Monai[a], T. Montini[a], J. Luo[b], E. Fonda[c], T. Duchon[d], M.M. Khader[e], V. Matolin[d], C.B. Murray[f], R.J. Gorte[b], P. Fornasiero[a]

[a]Department of Chemical and Pharmaceutical Sciences ICCOM-CNR, Consortium INSTM Trieste Research Unit, University of Trieste, via L. Giorgieri 1, 34127 Trieste (Italy); [b]Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 311 A Towne Building, 220 South 33rdStreet, Philadelphia, PA 19104 (USA);[c]SAMBA beamline, Synchrotron SOLEIL, L'Orme des Merisiers, S. Aubin BP48 91192 (France); [d]Charles University in Prague, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, V Holešovičkách 2, 18000 Prague, Czech Republic; [e] Gas Processing Center, College of Engineering, Qatar University, Doha, P.O. Box 2713, Qatar; [f]Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104 (USA)
e-mail: matteo.monai@phd.units.it

The world is facing an era of global environmental pollution, as a result of the tremendous population growth and the consequent massive fossil fuel-based energy consumption. A significant exploitation of renewable energies is needed to guarantee quality of human life and allow further sustainable growth, but this may take decades to happen. In order to mitigate the negative effect of human activities on the environment in the short- and mid-term, the development of more efficient technologies for emissions abatement and for renewable fuels production is imperative. Heterogeneous catalysis and photocatalysis are two key pillars of a multi-approach strategy to solve these issues. Exploiting the tools of nanotechnology, tailored nanostructured materials can now be produced, which show different properties in comparison to their bulky counterparts, often resulting in better catalytic performances. Combining the elements of the periodic table in nano-alloys allows to expand the possibility of catalyst generation. Consistently with these approaches, well-defined nanostructured materials were synthesized and characterized for environmental and energy-related applications, such as emissions control, biofuels synthesis and photocatalytic H_2 production. It is shown that structural control at the nanoscale is a great instrument for understanding reaction pathways, for studying the nature of catalytic active sites, and for synthesizing more selective, active and stable catalysts.Two synthetic strategies were followed to acquire nanostructural control: a self-assembly method was employed to prepare hierarchical materials starting from functional nanoparticles (1), and advanced solvothermal methods were used to prepare monodisperse nanocrystals having controlled size and composition (2-4). State-of-the-art hierarchical Pd-based catalysts embedded by metal oxide promoters were tested for methane catalytic oxidation in the presence of poisoning compounds typically found in real applications, such as H_2O, SO_2 and phosphates (5-7). Detailed surface studies allowed to propose deactivation mechanisms and strategies to improve catalysts resistance to deactivation. Well-controlled nanostructured Pt-based alloys and Ni-Cu alloys showed improved activity, stability and selectivity for hydrodeoxygenation reactions of biomass-derived feedstocks to produce biofuels (2-4).The control of nanostructure was pivotal to understand the reason for such enhanced performances.All these findings greatly contributed to the development of catalytic materials for energy-related applications.

References

1. M. Cargnello *et al.*, Science, 2012, 337, 713-717.
2. J. Luo *et al.*,ACS Catalysis 2016, 6 (7), 4095-4104.
3. J. Luo, *et al.*, Appl. Cat. B - Environ. 2016, 199, 439-446.
4. Monai, M *et al.*, Catal. Sci. Technol., 2017, 7, 1735-1743.
5. M. Monai *et al.*, Chem. Cat. Chem., 2015, 7, 2038-2046.
6. M. Monai *et al.*, Appl. Cat. B - Environ. 2016, 197, 271-279.
7. M. Monai *et al.*, Appl. Cat. B - Environ. 2017, 202, 72-83.

DFT-D study of crystal phase transitions in syndiotactic polypropylene
Premio Tesi di Laurea

Massimo C. D'Alterio[a], *Ana B. Muñoz-García*[a], *Finizia Auriemma*[a], *Claudio De Rosa*[a], *Michele Pavone*[a]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Via Cintia 26, 80126, Napoli, Italia; E-mail: massimochristian.dalterio@unina.it*

Syndiotactic Polypropylene (sPP) is a semi-crystalline polymer, which exhibits an uncommon mechanical behaviour: after a mechanical stress, as an axial elongation, sPP recovers its initial length at the equilibrium. This elastic behaviour has an enthalpic driving-force, unlike common amorphous elastomers where driving-force is entropic. The reason behind this phenomenon is a first order transition between two different crystalline forms. In the unstrained phase (Form II), macromolecular chains of sPP are helices with **s**(2/1)2 symmetry, whereas by stretching the polymer they adopt a trans-planar conformation with **t***cm* symmetry, where they constitute a crystalline phase stable only under stress (Form III) (1). Much is known about these two forms, less about molecular mechanism of the transition from form II to III (Figure 1).

The main goal of this work is the characterization of the mechanism: we investigate the intermediates structures, the transition states and the related energetic barrier. For this purpose, the survey method is based on computational chemistry: in fact atomistic simulations provide a computationalmagnifying glass to follow atoms and chain movements along the transformation. In particular, we implemented an *ab initio* simulation strategy, based on density functional theory (2) (DFT-GGA) including a D3 correction to take into account dispersion forces among the sPP chains in the crystal (3). In order to confirm and examine in depth theoretical results, an experimental study of the morphology of stretched fibers after relaxations has been carried on.

In conclusion, by integrating theoretical and experimental results, we got proofs about the transition mechanism and we depicted new insights on structure-properties relationship in semi-crystalline polymers.

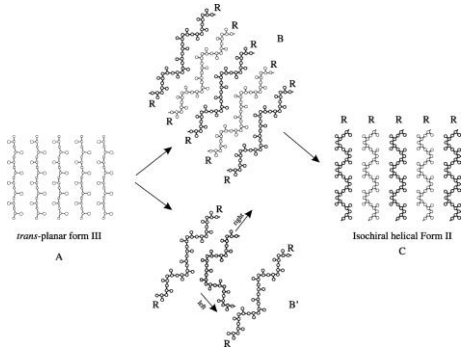


Figure 1. A possible transition pathway

References

1. C. De Rosa, F. Auriemma, *Prog. Polym. Sci*. 2006, **11**, 145-237.
2. P. Hohenberg, W. Kohn, *Physics Review* 1964,**136**, B864-B871.
3. V. Barone, M. Pavone *etal., J. Comput. Chem.* 2009, **30**, 934-939.

Development of nanostructured nickel based catalysts for hydrogen production Premio Tesi di Laurea

Cristina Pizzolitto

Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM RU of Venice, via Torino 155, I-30172 Venezia Mestre, Italy

Energy is world driving force because it controls every human activity and brings the population the possibility of a better future. Nowadays, most energy requirement relies on fossil sources like coal, oil and natural gas, that are still cost-effective (1). These sources, however, suffer environmental, social and economic issues. Hydrogen is the most promising fuel because it's a clean source, water is the only co-product of its combustion, it's nontoxic and it can be employed inside fuel cell enginesto obtain electrical energy directly from chemical bonds. One of the most promisingand efficient processesto produce hydrogen is ethanol steam reforming (ESR) for the high H/C ratio that makes ethanol a good feedstock. In particular, ethanol can be obtained from the fermentation of biomass,as clean and sustainable source,avoiding the use of fossil fuels. In addition to this, CO_2, a noxious by-product, finds application in other technologies. For example, another process that can be used to produce hydrogen, taking advantage of two of the main greenhouse gasses, is methane dry reforming (MDR).

The aim of this work is the development of heterogeneous nickel based catalytic systems that are active and versatile for both the reactions of ESR and MDR.

Nickel was chosen for its high activity to break carbon-carbon bond and for its inexpensiveness compared to noble metal but, due to its low thermal stability toward sintering and coke resistance, the role of support is crucial to minimize metal sintering and coke poisoning. Ceria was chosen for high redox properties, while zirconia for its elevated mechanical and thermal stability (2). Both have some limitations that can be overcome introducing lanthanum oxide. Indeed, this promoter could enhance redox ability of ceria and reduce acidity of zirconia (3). Aimed at optimizing support-promoter interaction and maximize their synergistic effect, the method of lanthanum oxide introduction was studied too. Lanthanum oxide was added to the support by two different synthetic approaches: via impregnation and co-precipitation.

It was found that lanthanum oxide is a good promoter both for ceria and zirconia catalysts because an increase in activity and stability was observed for both ESR and MDR. The introduction method was fundamental in order to achieve the maximum interaction between support and lanthana, in particular for ceria support. In fact, for this system, it was observed that co-precipitation method is the best technique to increase ceria redox properties, as confirmed by XRD analysis. On the contrary, for zirconia one, the introduction method has not been considered fundamental because the effect of lanthanum oxide is ascribed at its basic ability. In conclusion, with the addition of lanthanum oxide on nickel ceria and zirconia catalysts it was found a versatile catalytic system that works for both the different reactions of ethanol steam reforming and methane dry reforming.

References

1. E. Fostera, M. Contestabileb, J. Blazquez, B. Manzano, M. Workmana, N. Shaha; Energy Policy 103 (2017) 258-264.
2. P. Osorio-Vargas, C. H. Campos, R. M. Navarro, J. L.G. Fierro, P. Reyes; Journal of Molecular Catalysis A: Chemical 407 (2015) 169-181.
3. H. Ma, L. Zeng, H. Tian, D. Li, X. Wang, X. Li, J. Gong; Applied Catalysis B: Environmental 181 (2016) 321-331.

Novel approaches towards the optimisation of metal nanoparticle basedcatalysts Premio Tesi di Dottorato

Sebastiano Campisi

Dipartimento di Chimica-Università degli Studi di Milano, Via Golgi, 19 20133 Milano; sebastiano.campisi@unimi.it

Catalyst design requires an improved understanding of the chemistry on the surface, a clear disclosure of the mechanism of the process and the ability to probe active sites under reaction conditions. This is possible if a knowledge-based approach is shaped around three pillars: 1) the controlled synthesis of nanomaterials; 2) theoretical modelling of materials that enable experimental results to be understood; and 3) *ex situ* and *in situ*characterization. These aspects have been examined in my Ph.D. thesis, focused on the optimization of supported noble metal based catalysts for liquid-phase oxidation processes. Two possible strategies for tailoring the selectivity in the base-free glycerol oxidation have been extensively investigated, by exploring the ability to orientate the reaction pathway towards the selective oxidation either of the primary alcohol function or the secondary alcohol function. The selective oxidation of the primary hydroxyl group in the glycerol molecule results in the production of glyceric acid. AuPt bimetallic nanoparticles, when supported onacidic supports, have been shown to be active and durable catalysts for the selective glycerol oxidation to glyceric acid under neutral conditions. Starting from these considerations we studied more in the detail the effect of surface acidity, by comparing various metal oxides with different type, number and strength of acid sites. We observed that the acid properties, especially the strength of H-bonding, are the key factor in tuning the selectivity. In the past years many efforts were devoted to switch the reaction pathwaytowards the oxidation of the secondary alcohol function, to maximize the yield of dihydroxyacetone (DHA), a high value-added product. Until now, best results in terms of DHA yield have been obtained using Bi-Pt/AC catalysts. However these systems suffer from quick deactivation due to metal leaching. We then examined the possibility to improve the durability of BiPt based catalysts by tuning the metal composition. In particular BiAuPt nanoparticles were supported on activated carbon and tested in base free glycerol oxidation. By comparing the catalytic performances of trimetallic AuPtBi NPs with the ones of bimetallic AuPt and BiPt NPs, we concluded that:I)the addition of Bi promotes the oxidation of the secondary OH function;II)the addition of gold enhances the catalyst stability, thus resulting in a good selectivity to DHA even at high conversion. Beside the metal composition and the surface properties of supports, also the preparation route can influence the catalytic performances of supported noble metal nanoparticles. The sol immobilisation technique, in which a protective agent (such as polyvinylalcohol, PVA) is used to stabilize metal nanoparticles, possesses advantages like the control of the metal particle size. On the other hand, the presence of residual protective agent can affect the catalytic performances. Using operando ATR-IR spectroscopy we revealed that, in the liquid phase benzyl alcohol oxidation, PVA produces a selectivity enhancement to benzaldehyde limiting its decarbonylation. DRIFT experiments with CO as probe molecule allowed to relate this behavior to a specific blocking of Pd(111) facets which has been recognized to facilitate the decarbonylation step. In an ideal knowledge-based approach experimental evidences should be supported by theoretical results. For this reason, the last part of my Ph.D. was devoted to the application of Density Functional Theory modelling to the investigation of some of those features experimentally investigated. Promising preliminary results revealed that the local structure and composition of active site play a crucial role in affecting the reaction mechanism of ethanol oxidation. In particular the presence of oxygen and defects strongly modify the reaction mechanism from an energetic point of view. Concluding, the design of supported noble metal nanoparticle based catalysts can be optimized by using a novel approach, which takes into account and harmonizes all the different aspects involved in the process.

Sustainable catalytic processes for the synthesis and use of organic carbonates Premio Tesi di Dottorato

Tommaso Tabanelli

C.I.R.I.-E.A., Viale del Risorgimento 4, Bologna, 40136, Italy

The present study is focused on the development and improvement of sustainable catalytic processes for the synthesis of organic carbonates (OCs). These compounds are among the most promising green alternatives for the replacement of conventional toxic solvents and fuel additives and for the development of innovative intermediates in the pharma and polymer industries(1,2). Thedirect condensation reaction between carbon dioxide and several alcohols and diols was investigated using a new generation of mesoporous nanosilicas functionalized by insertion of amino groups (3). Unfortunately, these reactionssuffer from strictly thermodynamic limitations and lead to very poor carbonates yields. Afterward, the carbonate interchange reaction (CIR) of the simplest linear organic carbonate, dimethyl carbonate (DMC), with several alcohols has been investigated in order to synthesize higher carbonates. Indeed, in the CIR one carbonate is converted into another one, because one or both of the acyl-oxygen moieties of the parent carbonate are displaced by an appropriate alkoxide/aryl oxide(4). However, these are equilibrium-limited reactions, often with low equilibrium constants, especially when used for the synthesis of aromatic carbonates. In order to solve this problem, complex reactive distillation systems (RDS) are usually applied for enhancing the removal of the lightest co-product of the reaction: methanol. Nevertheless, the formation of a complex azeotrope between methanol and DMC leads to important losses of this reagent during distillation, that finally are detrimental for the reaction. Therefore, the development of an innovative lab-scale implemented RDS, based on the selective adsorption of methanol from the distilled mixture inside appropriate molecular sieves was envisaged, accompanied by continuous recovery of DMC into the reaction mixture. In this way, a continuous and efficient in-situ removal of methanol (co-product of the reactions) with negligible losses of DMC was accomplished, shifting the reaction equilibriums and allowing to obtain yields considerably higher than the equilibrium values. The application of this method in the synthesis of catechol carbonate (CC), combined with the optimization of the isolation and purification steps, allowed us to obtain an isolated yield of 90% of this scarcely investigated compound. The obtained CC was investigated as an alternative, more efficient carbonate source for the selective synthesis of a wide plethora of both dialkyl and alkylene carbonates (e.g glycerol carbonate, GlyC), in the presence of a basic catalyst. Indeed, results obtained under very mild reaction conditions (40-80°C, ambient pressure) and low reaction time (30 to 60 min) proved the unprecedented outstanding potential of CC, that not only greatly enhanced the reaction kinetics, but also promoted the quantitative formation of symmetric carbonates ($ROCO_2R$), these products being elusive in the CIR of both EC and DMC(5). The obtained GlyC has been also used as innovative chemical intermediate, for the condensation reaction with catechol in order to obtain the efficient synthesis of 2-hydroxymethy-1,4-benzodioxane (HMB) an important intermediate for the pharma industry. Finally, some of the synthesized carbonates were tested for the gas-phase phenol alkylation showing an interesting reactivity that could be properly modulated by changing the reaction conditions and the catalyst acid-base properties.

References

1. J.H. Clements, Ind. Eng. Chem. Res. 2003, 42(4), 663-674.
2. B. Schaffner, S. Schaffner, S. P. Verevkin and A. Borner, Chem. Rev., 2010, 110, 4554-4581.
3. V. Crocellà, T. Tabanelli, Jenny G. Vitillo, Daniele Costenaro, Chiara Bisio, Fabrizio Cavani, Silvia Bordiga.Applied Catalysis B: Environmental 2017,211 323–336.
4. A. A. G. Shaikh, S. Sivaram, Chem. Rev., 1996, 96, 951-976.
5. T. Tabanelli, E. Monti, M. Selva, F. Cavani. Green Chem., 2017,19,1519–1528.

n-butane to maleic anhydride: an impossible reaction and a catalyst which does miracles Premio Mario Giacomo Levi

Fabrizio Cavani[a], *Mario Novelli*[b]

[a] *Dipartimento di Chimica Industriale "Toso Montanari", ALMA MATER STUDIORUM Università di Bologna, Viale Risorgimento 4, 40136 Bologna;*
[b] *Polynt SpA via E. Fermi 51, Scanzorosciate (BG);*
fabrizio.cavani@unibo.it; mario.novelli@polynt.com

The production of maleic anhydride is carried out by means of the gas-phase selective oxidation of *n*-butane. This reaction still represents the most significant example of valorisation of a natural-gas component by transformation into an added-value intermediate chemical. It is carried out in industry by means of various technologies, amongst which one of the most advanced is the fluidized-bed process jointly developed by Lummus (today CBI) and Lonza (today Polynt) in the 80's (ALMA process). The catalyst is the key component of this technology; it allows the direct (one-pot) transformation of a saturated molecule, which is an unconventional reactant due to the absence of any functional moiety, into an unsaturated anhydride by means of a reaction which formally involves several steps with the exchange of 14 electrons in overall. Indeed, this reaction is regarded as "impossible to do" based on conventional reactions taken from Organic Chemistry textbooks. The catalyst which is able to perform this "miracle" is based on vanadyl pyrophosphate, $(VO)_2P_2O_7$; it was discovered in the 60's, and soon became a star in the field of catalytic selective oxidation.
Polynt SpA and the "Catalytic Processes Development Team", Bologna University, have been studying the vanadyl pyrophosphate catalyst since the 90's, with a twofold aim: (a) understand the key features of catalyst and the reaction mechanism, and (b) develop more efficient catalysts to implement for the ALMA process. The successful collaboration between Polynt SpA and Bologna University allowed the development of 4 generations of improved catalysts along the years, with an overall increase of MA yield of more than 10%, increased catalyst stability, and decreased catalyst consumption[1]. A detailed study of the nature of active sites, carried out by combining reactivity experiments with *in-situ* spectroscopic techniques, allowed us to develop an in-depth understanding of the characteristics of active sites in vanadyl pyrophosphate, which finally turned out to be the winning strategy for innovation from both a scientific and an industrial viewpoint[2].

References

1. EP 0804963 B1; US 6734135 B1; EP 1517748 A1; EP 1514598 A1.
2. F. Cavani, S. Luciani, E. Degli Esposti, C. Cortelli, R. Leanza, *Chem. Eur. J.***16** (2010) 1646-1655; A. Caldarelli, M. A. Bañares, C. Cortelli, S. Luciani, F. Cavani, *Catal. Sci. Technol.***4** (2014) 419-427.

Conferenze su Invito

- INDIL01: Gaetano Iaquaniello, KT – Kinetics Technology SpA
- INDIL02: Amilcare Collina, MAPEI S.p.A.

What role will chemistry and chemical engineering play in creating a sustainable and prosperous word

Gaetano Iaquaniello

KT – Kinetics Technology SpA, Viale Castello della Magliana 27, 00148 Roma;
e-mail: G.Iaquaniello@kt-met.it

Cleaner water, fuels and energy; safer food; more consumer goods, effective medicines and medical devices; more efficient materials from automobiles to rocket ships. These are going to be global challenges which the chemical industry is going to face in the next 30-40 years.
How such issues could be addressed in a sustainable way? Without compromising the ability of future generation to meet their own needs. Society currently has a non-sustainable dependence on a finite supply of fossil-fuels-based hydrocarbons used in almost every synthetic material in our economy. The growth in energy demand is projected to continue and the cumulative impact of burning fossil fuel to meet this demand raises serious concerns (green house effect). In a transitional period the CO2 need to be recovered and reused. New and more efficient methods to activate inert molecules as H20 and CO2 are required to offset the conventional methanation process. CO2 conversion to olephines could be a valid alternative. With price of oil and gas at today levels the quest for renewable feedstocks, green products and processes is becoming harder and harder if we want to maintain a prosperous world. How in this contest we are going to face middle-class growth in the developing world which is going to spur massive demand?
My view point presentation will try to give a contribution by focusing on basic research in energy and energy conversion, green chemistry and processing, environment and last but not least education which will play a central role in the quest for sustainability. A waste-to-chemicals process will be illustrated as an example of how alternative feedstocks can be used to make bulk chemical productions as methanol or urea with fewer unwanted by-products.

Materials chemistry for sustainable buildings: a review of MAPEI technologies

Amilcare Collina

MAPEI S.p.A. Via Cafiero 22 20158 Milano

This lecture will refer to the contribution of materials chemistry to the sustainability of existing buildings, for which energy efficiency and seismic resistance are key factors.

1. Energy efficiency

In Italy at 2011, the date for the last ISTAT census, buildings for residential use amounted to 12.2 million, with more than 31 million homes. A large part of them, more than 45 years old, record annual consumption from a minimum of 160 kWh/m^2 to over 220 KWh/m^2.

Looking at nonresidential sector, the assets used by the Public Administration amount to approximately 420 million square meters, of which about 100 million m2 would require urgent renovation.

As far as the improvement of the energy efficiency is concerned, the most effective solutions proposed by chemical industry are the materials for thermal insulation, the phase change materials and the materials for window frames.

The External Thermal Insulation Composite System MAPETHERM®, proposed by MAPEI, will be described. The ETICS system, applied on the peripheral walls of the building, allows to reach significant energy savings, to improve the living comfort and to reduce the mechanical stress of the building structures.

2. Seismic risk

Almost half the Italian territory is at high risk of earthquakes. Three are the regions where the building heritage is exposed to greater seismic risk: Sicily (2.5 million homes), Campania (2.1 million homes), Calabria (1.2 million). Looking at nonresidential buildings, over 24,000 schools and 1,800 hospitals are located in highly seismic areas.

As far as the seismic risk mitigation is concerned, a number of technologies have been already developed by the chemical industry, both for structural reinforcement and nonstructural elements.

The technologies make use of fiber or tissue composite materials with polymeric matrix as well as cement based matrix.

The following technologies developed by MAPEI will be described:

- MAPEI FRP SYSTEM: Structural strengthening system comprising high strength and very high strength fibers (carbon, glass, steel or basalt) and epoxy matrixes specially formulated for the application to structures made from reinforced concrete, steel, masonry or wood.
- MAPEI FRG SYSTEM: A complete range of composites which, unlike traditional FRP, uses an inorganic, pozzolanic binder to guarantee excellent physicochemical and mechanical compatibility with masonry substrates (stone, bricks and tuff) as well as with reinforced concrete.
- MAPEI EQ SYSTEM: a protection system for internal and external secondary partition walls which stops walls collapsing or tipping over during seismic activity.
- PLANITOP HPC: High Performance Micro-Concrete, with extremely high compressive strength, characterized by its capability to absorb high fracture energy.

The already mentioned technologies give a significant contribution to the sustainability of the existing building heritage.

Comunicazioni Orali

CO_2 photoreduction at high pressure to both gas and liquid products over titanium dioxide: the effect of unconventional reaction conditions

Elnaz Bahadori[a], Matteo Compagnoni[a], Antonio Tripodi[a], Laura Prati[a],Carlo Pirola[a], Gianguido Ramis[b], Ilenia Rossetti[a]

[a]Dip. Chimica, Università degli Studi di Milano and INSTM Unit Milano-Università, Milan, Italy
[b]Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, Genoa, Italy
elnaz.bahadori@studenti.unimi.it; ilenia.rossetti@unimi.it

The photoreduction of CO_2 is an intriguing process, which allows the synthesis of fuels and chemicals. One of the limitations for CO_2 photoreduction in the liquid phase is its low solubility in water. Several studies have been proposed during the last years in order to enhance the photocatalysts performance and improve the phototreactors for this purpose (1, 2). This point has been here addressed by designing a fully innovative concept of pressurized photoreactor, allowing operation up to 20 bar and applied for the first time to improve the productivity of this very challenging process (3-5). The photoreduction of CO_2 in the liquid phase was performed using the commercial TiO_2 (Evonink P25) in the presence of Na_2SO_3 as a hole scavenger. The different reaction parameters (temperature, working pressure, pH) and various catalysts have been considered for investigation of productivity and selectivity in the gas and liquid phase. The expected and formed products in liquid phase in the constant pressure and temperature and in the course of reaction time were formic acid and formaldehyde, respectively. Moreover, for longer reaction time, gas phase products formed (H_2 and CO with no trace of methanol or methane) after accumulation of significant amount of organic compounds in the liquid phase. The formation of gas products takes place within two parallel reaction pathway: i) CO_2 photoreduction into formic acid which may further photoreduce to formaldehyde and finally evolve into CO/CO_2+H_2 (photoreforming), ii) enhancing the CO_2 dissolution in the water by addition of a base with formation of carbonates (pH= 12-14) resultedin the reduction of carbonates to formaldehyde and consequently formed CO/CO_2+H_2 in the gas phase through photoreforming. In order to improve visible light absorption and increase the lifetime of the photogenerated charges, Au was loaded on TiO_2 (0.1-0.5 wt%)by a deposition-precipitation method. Methanol and methane were the main products in liquid and gas phase, respectively, demonstrating the higher reactivity of catalyst in the present of Au. Increasing the Au loading from 0.1wt% to 0.2 wt% improved the productivity toward methanol and methane in liquid and gas phase, respectively. However, further increasing in metal loading negatively affected the Au dispersion and catalyst surface area and resulted in lower H_2 productivity. Furthermore, testing parameters, such as temperature and pressure directly affected the products formation. Increasing the pressure favored the liquid products accumulation was detrimental for H_2/CH_4 productivity. On the other hand, increasing the temperature, decreased the CO_2 solubility in the water, but enhanced the kinetics and mass transfer leading to the formation of H_2/CH_4.

Acknowledgements: Fondazione Cariplo (grant 2016-0858 “UP – Unconventional Photoreactors”) is gratefully acknowledged.

References

1. Yamashita H., Fujii Y., Ichihashi Y., Zhang S.G., Ikeue K., Park D.R., Koyano K., Tatsumi T., Anpo M., 1998, Catalysis Today, 45, 221.
2. Anpo M., Yamashita H., Ichihashi Y., EharaS., 1995, J. Electroanal. Chem, 396, 21.
3. Rossetti I., Villa A., Pirola C., Pratia L., Ramis G., 2014, RSC Adv, 4, 28883.
4. Rossetti I., Villa A., Compagnoni M., Prati L., Ramis G., Pirola C., et al., 2015, Catal. Sci. Technol, 5,4481.
5. Galli F., Compagnoni M., Vitali D., Pirola C., Bianchi C.L., Villa A., Prati L., Rossetti I., 2016, App Catal B: Environmental, 200, 386.

How structural and surface properties affect stability of hybrid CuZnZr-zeolite catalysts during DME synthesis via CO_2 hydrogenation

Giuseppe Bonura[a], *Catia Cannilla*[a], *Fabio Costa*[a], *Aldo Mezzapica*[a], *Francesco Frusteri*[a]

[a] *CNR-ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Messina, 98126, Italy; email: giuseppe.bonura@itae.cnr.it*

The production of dimethyl ether (DME) by hydrogenation of CO_2 is an issue that recently is receiving a particular attention (1-6) As well known, in order to hydrogenate CO_2 it is necessary that catalyst possesses a multi-functionality suitable to activate both CO_2 and $H_2$and also to dehydrate methanol (MeOH) into DME (3,4,6). In general, MeOHis first generated by interaction of activated H_2 and CO_2 on metal and oxide sites respectively, while DME is then formed by MeOH dehydration on acid sites (1-6).

Recently, we paid attention on the preparationof novel hybrid CuZn-Zr–zeolite catalytic systems,so that the multi-functionality necessary for the reaction is grain-to-grain ensured. Catalytic results, in terms of CO_2 conversion and product distribution using a fixed bed reactor in several reaction conditions (T_R: 200-260 °C; P_R: 3.0 MPa, *GHSV*: 2,200-8,800 *N*L/kg$_{cat}$/h) allowed to ascertain asthe homogeneous distribution of neighbouring metal-oxide-acid sites significantly enhances the rate of mass transfer, sofavouring the achievement of high DME yield.

In the attempt to better assess the potential of such hybrid materials as very promising catalysts for the production of DME via CO_2 hydrogenation, in this work we performed several durability tests (tos, 30 h) at 260°C, 3.0 MPa and 2,200 *N*L/kg$_{cat}$/h of a mixture $CO_2/H_2/N_2$ (3/9/1), in presence of CuZnZr-FER systems containing home-made zeolites with a bidimensional framework (ferrierite topology) at variable acidity (Si/Al ratio: 8-60).

Catalytic data showed a not negligible decrease both in the CO_2 conversion and in the DME selectivity especially in the first 10 h of reaction, mostly evident on the systems containing a more acidiccharacter. Considering that no coke was detected on the "deactivated" catalysts, the plausible explanation about the observed trend was ascribed to the water formation that, absorbing on acid sites, inhibits the dehydration reaction, also leading to a rearrangement of oxide clusters with significant enlargement of metallic Cu particles, probed by N_2O chemisorption measurements that evidenced a considerable shrinkage in the copper surface area as a direct proof of metal sintering.

References

1. G. Bonura, M. Cordaro, L. Spadaro, C. Cannilla, F. Arena, F. Frusteri, Appl. Catal. B: Environ. 140–141 (2013), 16–24.
2. F. Frusteri, M. Cordaro, C. Cannilla, G. Bonura, Appl. Catal. B: Environ. 162 (2015) 57-65.
3. F. Frusteri, G. Bonura, C. Cannilla, G. Drago Ferrante, A. Aloise, E. Catizzone, M. Migliori, G. Giordano, Appl. Catal. B: Environ. 176-177 (2015) 522-531.
4. G. Bonura, F. Frusteri, C. Cannilla, G. Drago Ferrante, A. Aloise, E. Catizzone, M. Migliori, G. Giordano, Catal. Today 277 (2016) 48–54.
5. G. Bonura, C. Cannilla, L. Frusteri, A. Mezzapica, F. Frusteri, Catal. Today 281 (2017) 337–344.
6. F. Frusteri, M. Migliori, C. Cannilla, L. Frusteri, E. Catizzone, A. Aloise, G. Giordano, G. Bonura, J. CO2 Util. 18 (2017) 353-361.

Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol

Filippo Bossola[a], *Xavier Isidro Pereira-Hernández*[b], *Claudio Evangelisti*[a], *Yong Wang*[b,c], *Vladimiro Dal Santo*[a]

[a] *CNR – Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133 Milano, Italy;*
[b] *The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States;*
[c] *Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington 99354, United States; filippo.bossola@istm.cnr.it*

Hydrogen is regarded as a clean energy vector suitable to replace the common fossil fuels. In order to achieve a production of fully green hydrogen, renewable feedstock, like biomass, should be used (1). Due to the complex nature of biomass, however, model molecules are mostly used in reforming reactions for hydrogen production. The addition of a promoter is often used to improve the performances of the catalyst (2). While the promoting effect of many noble metals has been elucidated, the precise impact on the surface features as well as on the reaction pathways of non-noble metals is still unclear. In this work, a Pt-based catalyst was modified by the addition of a Mn promoter, and tested in the steam (SR) and aqueous reforming (APR) of glycerol, which was chosen as model molecule of polyols and as by-product of the bio-diesel industry (3). The reactions were carried out at 225 °C with 10 wt.% glycerol aqueous solution. The presence of Mn had a major impact on the catalyst, mostly reflected in the SR reaction, with an increase in hydrogen productivity and total conversion of factors of 3 and 4, respectively. A weaker promoting effect was found in the APR reaction, with enhancements factors of 1.3 and 1.4. A thorough characterization of the catalysts was performed by mimicking the real working conditions, that is by treating the samples with steam at the reaction temperature. The addition of Mn introduced peculiar surface acidic sites in the form of few, strong Lewis acid sites, as detected by ammonia temperature programmed desorption experiments and attenuated total reflectance infrared analyses using pyridine as probe molecule. These sites, likely generated by exposed $Mn^{\delta+}$ sites in close proximity to Pt sites, contributed to the activation of the glycerol molecule. In fact, at comparable conversion levels, the hydrogen productivity of the bimetallic Pt-Mn/C catalyst outperformed the Pt/C catalyst (Figure 1). Under APR conditions, the promotion of Mn was exerted in a different way. Although the improvement in hydrogen productivity and conversion were lower than in SR, the selectivity toward hydrogen was increased. Moreover, most of the Mn leached out. These findings can be explained by the formation of an alloy between Mn and Pt, which prevented some of the Mn to be leached and promoted the CO spillover from the Pt sites (4). In fact, the C-O bond cleavage activity of the catalyst was not significantly altered, whereas under SR conditions was favoured at the expenses of the C-C cleavage. With this study, we made a significant step forward the comprehension of the actual promoting mechanism of non-noble metals on catalysts for reforming reactions, but much still needs to be done, especially when using harsh reaction conditions, like those of APR (5).

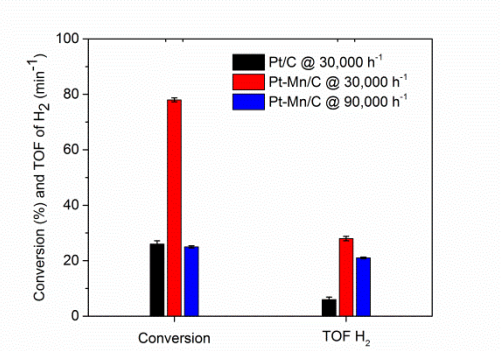


Figure 1. Catalytic performances of Pt/C and Pt-Mn/C in SR of glycerol.

References

1. G. Marbán, T. Valdés-Solís, *Int. J. of Hydrogen Energ.*,**2006**, 32, 1625–1637.
2. V. Dal Santo, A. Gallo, A. Naldoni, M. Guidotti, R. Psaro, *Cat. Today*, **2012**, 197, 190–205.
3. C. A. G. Quipse, C. J. R. Coronado, J. A. Carvalho Jr., *Renew.Sust. Energ. Rev.*, **2013**, 27, 475–493.
4. Z. Wei, A. Karim, Y. Li, Y. Wang, *ACS Catal.*, **2015**, 5. 7312–7320.
5. F. Bossola, X. I. Pereira-Hernández, C. Evangelisti, Y. Wang, V. Dal Santo, *J. Catal.*,**2017**, 349, 75-83.

Selective arene production from aromatic ethers promoted by Pd/Fe_3O_4 catalyst under transfer hydrogenolysis conditions

Emilia Paone[a], *Rosario Pietropaolo*[a], *Francesco Mauriello*[a]

[a]*Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122 Reggio Calabria, Italy 1; emilia.paone@unirc.it*

The selective cleavage of C-O single bond preserving the aromatic nature represents one of the major challenges in the catalytic valorization of lignin [1].
In the last years, the co-precipitate Pd/Fe_3O_4 catalyst shown a powerful and efficient performance in the catalytic transfer hydrogenolysis (CTH) of lignocellulosic platform derived molecules. [2-4]
In this context, the selective cleavage of the C–O bond of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE) - as model compounds of lignin linkages – was investigated, under CTH conditions using 2-propanol as the H-donor and the Pd/Fe_3O_4 catalyst with a nominal palladium loading of 5 wt %.
The use of this catalyst, shown an appreciable BPE (0.1 M) conversion (19.7%) that increases by increasing the reaction temperature and, at 240°C, it is fully converted (100% conversion) into phenol and toluene as the only reaction products (100% aromatic yield) clearly indicating that the cleavage of the etheric C–O bond occurs as the primary reaction route under CTH conditions.
In the next step, the H-donor ability of simple primary (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) and secondary (2-butanol, 2-pentanol and 3-pentanol) alcohols was tested and a tight relationship between the moles per l of aldehyde or ketone formed (H-donor ability) and the amount of BPE converted (moles per l) was observed. These results, coupled with the reactivity of the same pure alcohols in presence of the Pd/Fe_3O_4, suggest that the H-transfer from the alcohol and the hydrogen promoting the C-O bond breaking occur in a unique chemical process (Figure 1).
Reaction of PPE at 240 °C shows a lower conversion (22%) and 100% yield of aromatics. On the contrary, DPE was not converted at all. Interestingly, a linear correlation of the bond strength and the ability of the Pd/Fe_3O_4 catalyst in the CTH of aromatic ethers was found.
Therefore, the Pd/Fe_3O_4 catalyst is able to cleave the C–O bond of benzyl phenyl ether (BPE) and 2-phenethyl phenyl ether (PPE) under CTH conditions and, at the same time, avoid parallel hydrogenation reactions of the aromatic ring, being one of the most selective heterogeneous catalysts in the production of arene derivatives.

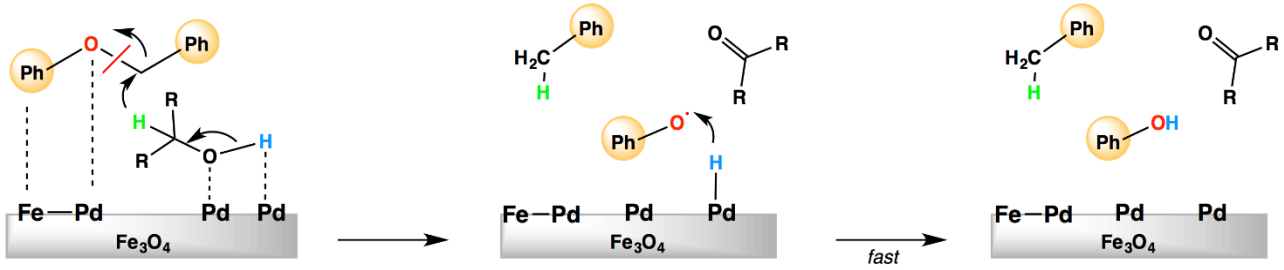


Figure 1. Pd/Fe_3O_4-catalyzed selective transfer hydrogenolysis of benzyl phenyl ether

References

1. G. Sergeev, J. F. Hartwig, Science, 2011, 332, 439-443.
2. C. Espro, B. Gumina, E. Paone, F. Mauriello, Catalysts, 2017, 7(3), 78.
3. M. G. Musolino, L. A. Scarpino, F. Mauriello, R. Pietropaolo, Green Chem., 2009, 11(10), 1511–1513.
4. E. Paone, C. Espro, R. Pietropaolo, F. Mauriello, Catal. Sci. Technol., 2016, 6, 7937.

Investigation of coating deposition and catalytic activation of periodic open cellular structures (POCS) by spin-coating

Riccardo Balzarotti[a], *Matteo Ambrosetti*[a], *Gianpiero Groppi*[a], *Enrico Tronconi*[a]

[a]*Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, Milano, 20156, Italy; riccardo.balzarotti@polimi.it*

The development of structured catalysts for process intensification is a topic of high interest in industrial research. A large variety of supports have been reported in literature, such as honeycomb monoliths, open cell foams, wire mesh and felts (1). Nowadays, novel manufacturing techniques enable the production of open cellular structures with periodic ordered geometry (POCS). In comparison with open cell foams, the control of the geometrical properties allows optimizing the structure towards the enhancement of heat and mass transfer rates and the reduction of pressure drops (2). Despite the huge interest in these supports, at present time, a little information is present in literature regarding their catalytic activation; in particular, a detailed description of washcoating process to achieve catalytically active supports is missing. In this view, the aim of this work is to fill this gap by providing a complete overview of the application of spin coating technique for catalytic medium deposition on POCS.In this work, aluminum POCS of cylindrical shape (9 mm diameter and 15 mm length) were used. The internal structure of the POCS has ideal cubic cell geometry; samples with constant strut thickness of 0.5 mm and different open cell sizes, namely 1.5, 1.75 and 2.5 mm, were tested. In the first part of the work, basic knowledge concerning wet coating layer formation and management on POCS was achieved. In particular, the effect of spin speed, spin time, liquid media viscosity and support properties (i.e. cell size and support length) were investigated. Coating load was found to decrease with the increase of spin speed and time (Figure 1-a) and promising results were obtained in terms of control of wet coating thickness.On the basis of this preliminary investigation, POCS were made catalytically active by depositing Pd/CeO_2 catalyst by slurry coating (3) and tested for the CO oxidation process. Good results were obtained in terms of CO conversion despite the small volume of the catalyst (Figure 1-b).

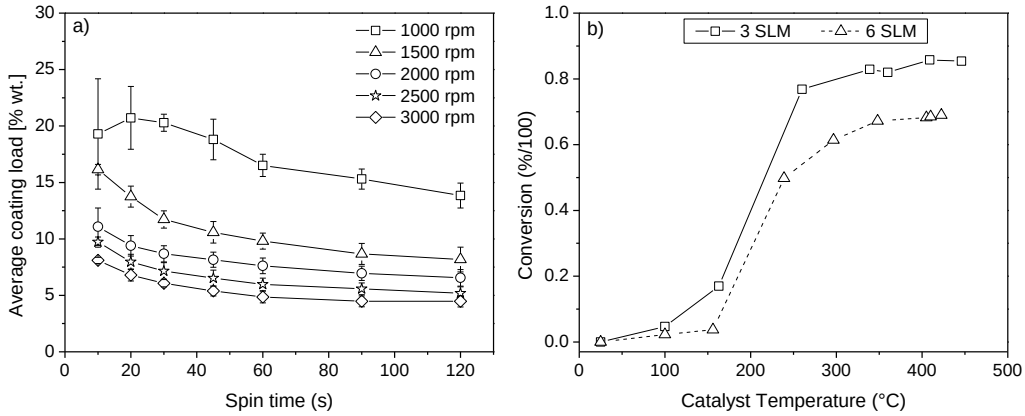


Figure 1. Coating dependence on spin speed and spin time for pure glycerol solution (a) and catalytic performance under CO oxidation process (b) for 1.75 mm cell size samples.

Thus, the use of spin-coating for washcoat deposition on POCS of different cell sizes was found to be a promising deposition technique, with remarkable advantages in washcoat layer management for the production of structured catalysts, enabling well adherent and catalytically active layers.

References

1. E. Tronconi et al., Curr. Opin. Chem. Eng., 5 (2014) 55-67.
2. E. Bianchi et al., Adv. Eng. Mater., 18 (2016) 608-614.
3. C. Italiano et al., Catal. Today, Cat. Today 273 (2016) 3-11.

Ethylene vinyl acetate: a promising binding material for high power-high energy electrodes with a prolonged cycle life

Pier Paolo Prosini[a], *Mariasole Di Carli*[a], *Livia Della Seta*[a], *Maria Carewska*[a], *Ivan Fuso Nerini*[b]

[a] *ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Via Anguillarese 301, 00123 Santa Maria di Galeria, Rome, Italy;e-mail: pierpaolo.prosini@enea.it*
[b] *VINAVIL S.p.A, via Valtellina, 63 - 20159 Milano – Italia; e-mail: i.fusonerini@vinavil.it*

The energy, the power, and the cycle life of a lithium-ion battery (LIB) are strictly related to the electrochemical characteristics of the active material. However, the binder used in the electrode formulation plays an important role since it influences the mechanical and electrical properties of the electrode (1). A suitable binder to be used in LIB technology must possess several characteristics such as high flexibility, good adhesion strength, and elevated electrochemical stability (2). In recent years there has been a gradual change in production technologies of electrodes moving from traditional electrodes based on fluorinated polymers (3) to new methods of preparation which employ water dispersible binder. The use of water-based emulsions, eliminating organic solvents necessary to dissolve the fluorinated polymers, makes the manufacturing of the electrodes an ecological process. Among the various polymers available on the market we selected ethylene vinyl acetatea hydro dispersible polymer largely used in the plastic industry, as a binder for the fabrication of the positive electrode of lithium-ion batteries. $LiNi_{0.5}Mn_{1.5}O_4$was used as the active material. The electrode was prepared by painting a thin aluminum sheet with a suspension obtained by mixing the carbon black, the active material, and the polymer in water. The electrode was first analyzed from a chemical-physical point of view. Thenthe anodic stability was examined versus a lithium anode. Finally the electrode was used to prepare a two electrodes lithium cell and the cell was tested to evaluate the electrode capacity retention as a function of the applied current and cycle number. The electrode has been found very promising for the realization of high energy, high power, long cycle life batteries being capable of cycling for hundreds of cycles with excellent performance and reduced loss of capacity.

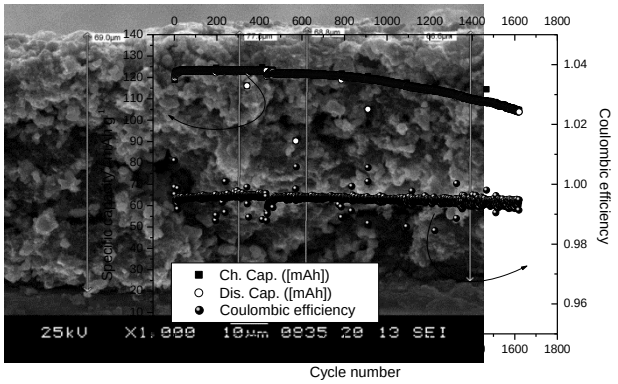


Figure 1. Left: high magnification SEM image of the cross section of the electrode. Right:Variation of the specific capacity and the Coulombic efficiency as a function of the cycle number

References

1. A. Gören,C.M. Costa,M.M. Silva,S. Lanceros-Méndez,Composites Part B: Engineering83 (2015) 333–345.
2. T. Yim,S.J. Choi,Y.N. Jo,T.-H. Kim,K.J. Kim,G. Jeong,Y.-J. Kim**,** Electrochim. Acta 136 (2014) 112–120.
3. B.P.N. Nguyen, N. Mariage, R. Fredon, E.M. Kelder, B. Lestriez, J. Electrochem. Soc. 162 (2015) A1451–A1459.

Unexpected viscoelasticity of Polydimethylsiloxane liquid blends

Vincenzo Villani[a], *Vito Lavallata*[a]

[a]*Dipartimento di Scienze,Università degli Studi della Basilicata, Campus Macchia Romana, Potenza, Italy; vincenzo.villani@unibas.it*

Recently (1), we showed that lightly crosslinked networks based on vinyl-terminated Polydimethylsiloxane (PDMS) liquid rubbers, have unusual rheological properties. In fact, it is observed a decrease of zero-shear viscosity $\eta_0$and viscoelastic moduli $G(t),G'(\omega)$ and $G''(\omega)$ with respect to pure polymer. The Unentangled Crosslinked Nanodomains (UCN) model was proposed in order to explain the rheological behaviour. At low concentration of curing agent, the formation of isolated crosslinked nanodomains is determined. At the nanodomains surface, the dynamics of short chains determines an entanglement-free interface, which contribute to the drop of the rheological properties. The viscoelasticity was explained by means the tube model theory and an extension of Einstein viscosity equation proposed.
Now (2), the same elastomers based on vinyl-terminated PDMS were used (Fig. 1).

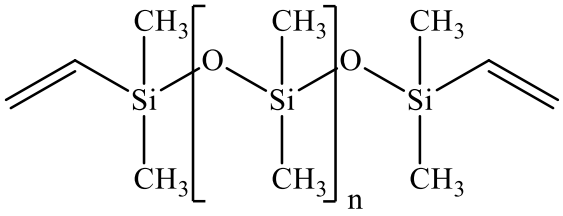


Figure 1. Liquid silicone rubber.

Liquid Silicone Rubbers (LSR, Dow Corning) at low, medium and high viscosity have been considered; low/high and medium/high viscous blends were prepared.
The rheometer DHR-2 (TA Instruments®) in a parallel plate configurationhas been used. To control the temperature from –15 to 150 °C, the instrument is equipped with a Peltier dispositive.
Pure components and their blends have been characterized in rotational and oscillating regime.Flow and viscosity curves, creep-and-recovery and stress-relaxationexperiments have been performed at 25 °C.
In oscillating regime, strain-frequency spectra have been carried out at 25 and 70 °C; dynamical-mechanical spectra from –15 to 150 °C performed, applying strain-frequency of 10 or 250 rad·s^{-1}.
The low/high blend exhibits an unexpected creep reduction and recovery increase with respect to high-viscous component.Surprisingly, the low-viscous component acts as a gelling-like agent reducing the compliance and enhancing the delayed elasticity (18% vs 7% for the high molecular weight precursor). Moreover, in the low frequency field, G'(ω) and G"(ω) increase with respect to the high-viscous component, corroborating the anomalous behaviour due to the low molecular weight component.
In order to explain the rheological behaviour, the tube model for the viscoelasticity of entangled polymer melts has been used.The viscosity decrease of the homopolymer blend should be ascribed to the reduction of the entanglement density, and the compliance drop and the increase of dynamic moduli due to the swelling of long chains by short ones, reducing the conformational flexibility.

References

1. V. Villani, V. Lavallata, Macromol. Chem. Phys.2017, *1700037*.
2. Submitted to Macromoles.

Molecular recognition and catalysis within confined space

Carlo Bravin[a], *Donato M. Mancino, Giulia Licini*[a], *Cristiano Zonta*[a]

[a]*Department of Chemical Sciences, University of Padova via Marzolo 1, 35131 Padova (PD) (Italy);carlo.bravin@studenti.unipd.it*

Biological containers and supramolecular cages have largely attracted the attention of scientists for their peculiar properties and applications.[1] These systems are characterized by defined internal cavities that have the fundamental functions to accelerate specific reactions with specific molecular targets, or as a transport containers. In particular we have recently reported a novel supramolecular cage built from the self-assembly of tris(2-pyridylmethyl)amine TPMA complexes that is able to perform molecular recognition of dicarboxylic acid.[2] The possibility to introduce multiple active metal sites having a non-saturated coordination sphere in the inner cavity of these objects open new frontiers in the field of molecular recognition and catalysis. In this communication we report the synthesis of an analogue cage synthesized from opportunely functionalized **TPMA** iron (II) complexes **1** that are already known to catalyze different oxidation reactions.[3] Initial attempts will show the efficiency of supramolecular cage 2 as catalyst respect to monomeric complex 1 in virtue of the confination of the reagents within the cavity.

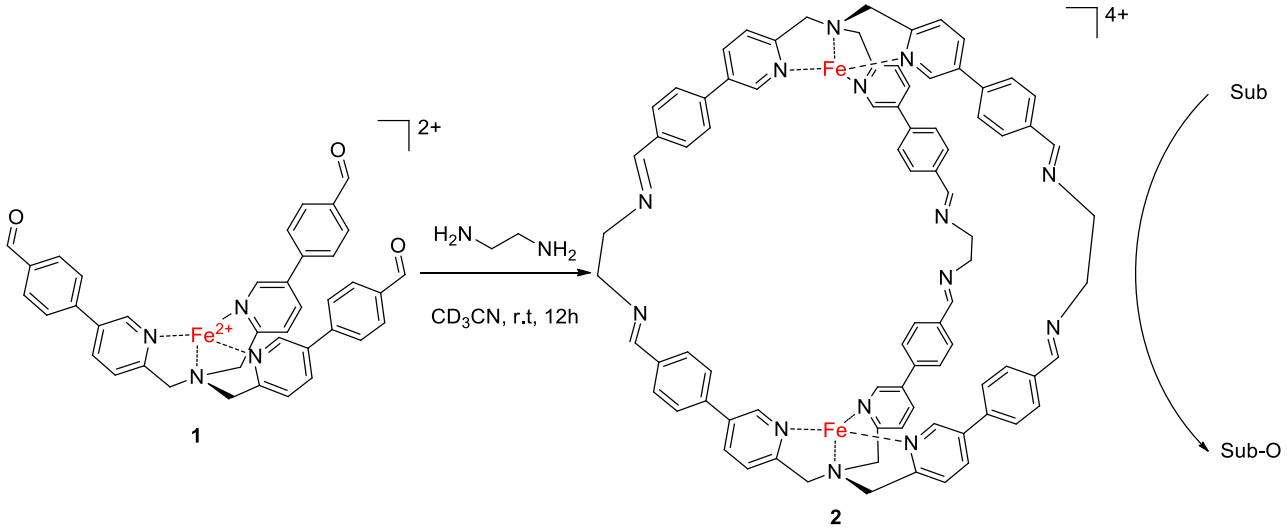


Figure 1. Synthesis of molecular cage 2 starting from complex 1. In all the structures, the counter anions are perchlorate.

References

1. Y.-T. Lai, D. Cascio and T.O. Yeates, *Science***2012***336*, 1129.
2. C. Bravin, E. Badetti, F.A. Scaramuzzo, G. Licini and C. Zonta, *J. Am. Chem. Soc*. **2017** doi:10.1021/jacs.7b0234.
3. C.Kim,K.Chen,J. and L. Que,*J. Am. Chem. Soc*. **1997** *119*, 5964.

Producing amino acid benzyl esters under ecofriendly conditions and without racemization

Cristiano Bolchi[a], *Francesco Bavo*[a], *Marco Pallavicini*[a]

[a]*Dipartimento di Scienze Farmaceutiche, via Mangiagalli 25, 20133 – Milano, Università degli Studi di Milano; cristiano.bolchi@unimi.it*

In the landscape of the constantly growing market of amino acids and derivatives, amino acid benzyl esters in unichiral form are high added value products of widespread use due to their multifaceted applications. Besides being starting materials for synthesis of unichiral active ingredients in pharmaceutical, cosmetic and food industry, they are important, often essential, intermediates in the chemical and chemoenzimatic synthesis of homo- and heteropolypeptides and, in particular, of dipeptides, a class of compounds having unique functions, unfindable in the constitutive amino acids. Therefore, it is rather surprising that, within the abundant literature on any scale preparations of amino acid benzyl esters, little or no attention has been, to date, devoted to three key issues in their productions. These are:
(a) the use of green or at least acceptable solvents in place of banned benzene, carbon tetrachloride and chloroform to azeotropically remove water resulting from the acid-catalyzed reaction of the unprotected amino acid with benzyl alcohol;
(b) the enantiomeric excess of the formed amino acid benzyl esters, which should be punctually measured because of the well-known susceptibility of amino acids and even more of their esters to racemize also under mild reaction conditions;
(c) the nature of the enantiomeric systems formed by the amino acid benzyl esters salts, which cannot be ignored because crystallization is the large-scale process generally used to recover and to purify these products.
Starting with a selection of amino acids (1,2,3) and then including further substrates, we have undertaken a comprehensive investigation on how to efficiently prepare a wide number of enantiomerically pure amino acid benzyl esters under scalable and ecofriendly conditions, namely by replacing banned solvents with green solvents. Chiral HPC and DSC strictly supported our investigation in order to select and to develop the best procedures, to recognize the unsuitable ones, to cleverly accomplish the benzyl esters salts crystallization and, lastly, to rationalize the very different inclinations to racemize shown by the tested amino acids.

References

1. C. Bolchi, E. Valoti, L. Fumagalli, V. Straniero, P. Ruggeri, M. Pallavicini *Org. Proc. Res. Dev.***2015**, *19*, 878-883.
2. C. Bolchi, *Chimica e l'Industria***2016**, *anno XCVIII (5-6)*, 4-6.
3. C. Bolchi, F. Bavo, M. Pallavicini *Amino Acids* **2017**, *49*, 965-974.

Microkinetic modeling of benzyl alcohol oxidation on Pd and AuPd catalysts

Alberto Villa[a], *Ilenia Rossetti*[a], *Laura Prati*[a], *Aditya Savara*[b]

[a]*Dipartimento di Chimica Università degli Studi di Milano via Golgi 19, 20133, Milano, Italy;*
[b]*Chemical Sciences Division Oak Ridge National Laboratory 1 Bethel Valley Road MS 6201, Oak Ridge, TN 37831;*
Alberto.Villa@unimi.it

The liquid phase oxidation of alcohols over supported metal catalysts, using molecular oxygen as the oxidant, has been extensively studied in the last decade (1). In particular, benzyl alcohol oxidation to benzaldehyde is of practical use for pharmaceutical, perfume, dye, and agricultural industries (2). Many studies have been reported on the noble metal, in particular Pd, catalyzed benzyl alcohol oxidation in presence of molecular oxygen (1). However, a complete mechanism of Pd catalyzed benzyl alcohol oxidation has not yet been proposed. Detailed mechanistic and chemical kinetic information are necessary to understand the process and for an industrial application of these catalytic materials.In this study, we have performed experiments in which the temperature, gas-phase oxygen pressure, and initial concentration of the benzyl alcohol were varied to elucidate the mechanism (3). Furthermore microkinetic modeling (simulation and fitting) of the reaction were performed (4,5).

The liquid-phase oxidation of benzyl alcohol was performed over Pd and AuPd nanoparticles supported on activated carbon. Experiments were performed in a batch reactor with para-xylene as the solvent and continuous gas purging of the headspace. From trends in the concentration profiles and integrated production of each product, it was determined that there are two primary reaction paths: A) an alkoxy pathway leading to toluene, benzaldehyde, and benzyl ether, and B) a carbonyloxyl pathway ("neutral carboxylate") leading to benzoic acid, benzene, and benzyl benzoate (3).

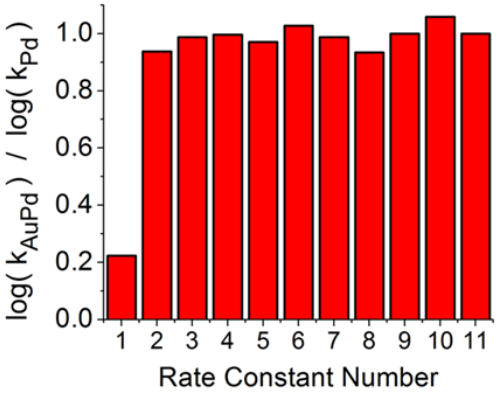


Figure 1. Ratios of the logs of the rate constants between AuPd/C and Pd/C, where the largest change on this scale was in k1 (5).

The microkinetic modeling in this work was able to reproduce the selectivities and trends observed for the production of both the main product (benzaldehyde) and the byproducts (benzene, toluene, benzoic acid, benzyl benzoate, and benzyl ether). The present study suggests that the most important activation energies are those of k2, k5, and k6 (Scheme 1), which we estimate as Ea_2=57.9 kJmol^{-1}, Ea_5=129 kJmol^{-1}, and Ea_6= 175 kJmol^{-1} corresponding to alcohol dissociation, alkyl hydrogenation, and reaction of alkyl species with alkoxy species. Under the same reaction conditions, AuPd/C has a lower activity compared to Pd/C and shows a different product distribution with less formation of products from the "carbonyloxyl" pathway (benzene, benzoic acid, benzoate). It was found that the selectivity changes can be explained by this change in k1, which corresponds to oxygen adsorption.

References

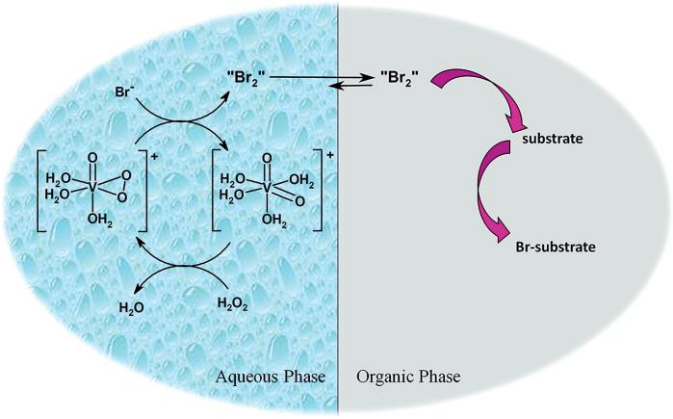
1. M. Besson, P. Gallezot, Catal. Today 2000, 57, 127-141.
2. T. Mallat, A. Baiker, Chem Rev 2004, 104, 3037-3058.
3. A. Savara, C. E. Chan-Thaw, I. Rossetti, A. Villa, L. Prati, ChemCatChem 2014, 6, 3464–3473.
4. A. Savara, I. Rossetti, C. E. Chan-Thaw, L. Prati, A. Villa, ChemCatChem 2016, 8, 2482 –2491.
5. A. Savara, C. E. Chan-Thaw, J. E. Sutton, D. Wang, L. Prati, A. Villa, ChemCatChem 2017, 9,253 –257.

Sustainable bromination of thymol: synthesis of new biologically active compounds

Federica Sabuzi[a,b], *Pierluca Galloni*[a,b], *Valeria Conte*[a,b]

[a]*Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica, snc, 00133 Roma*
[b]*BT-InnoVaChem srl, Via della Ricerca Scientifica, snc, 00133 Roma;*
federica.sabuzi@uniroma2.it

Vanadium peroxides, formed upon reaction between vanadium derivatives and hydrogen peroxide, are very effective oxidants of different substrates. Peroxido-vanadium complexes can oxide bromide ions to reactive species that can brominate organic substrates (1). This process mimics the activity of haloperoxidases enzymes (HalPO). Between them, vanadate dependent bromoperoxidase, a metal-enzyme containing vanadium (V) in the active site, catalyzes the oxidation of halide ions, such as bromide and iodide, by hydrogen peroxide (2). This activity is related to the formation of a peroxido vanadium species in the active site of the enzyme, which is a stronger oxidant than H_2O_2.
In this communication the oxidative bromination of thymol, a phenolic terpenoid compound main component of the *Thymus vulgaris* essential oilswill be presented. This "green" process occurs with no organic solvents, in very mild conditions and with sustainable reagents (3).



Importantly, biological tests showed that 4-bromothymol has a very high antimicrobial activity and low toxicity (4), so it can be used as a new active ingredient in several personal-care and home-care products.

References

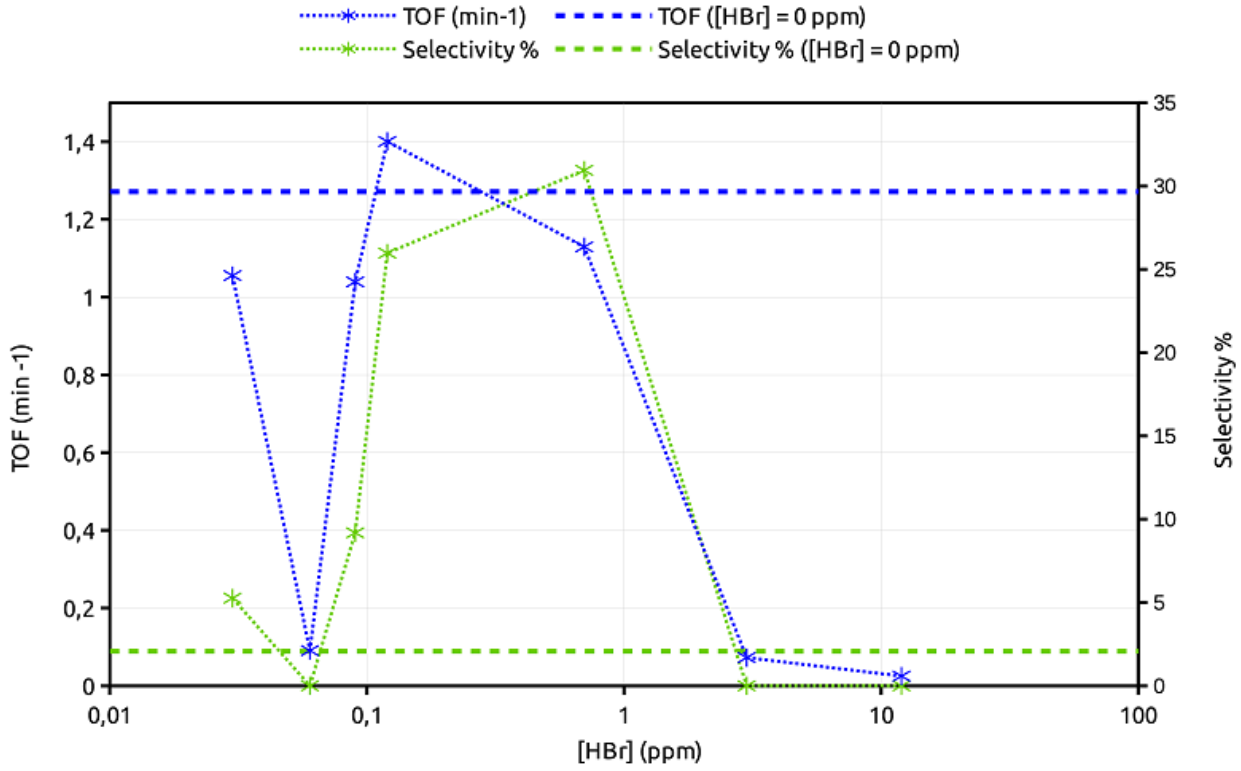
1. Conte V., Floris B., *Dalton Trans*., **2011**, *40*, 1419; Conte V., Coletti A., Floris B., Licini G., Zonta C., *Coord. Chem. Rev*., **2011**,*255*, 2165; Conte V., Coletti A., Mba M., Zonta C., Licini G., *Coord. Chem. Rev*., **2011**, *255*, 2345.
2. Wischang D., Hartung J., *Tetrahedron*, **2012**, *68*, 9456; Butler A., Carter-Franklin J. N., *Nat. Prod. Rep*., **2004**, *21*, 180.
3. Sabuzi F.,Churakova E., Galloni P., Wever R., Hollmann F., Floris B., Conte V., *Eur. J. Inorg. Chem*.,**2015**, 3519.
1. 4. Galloni P., Conte V., Sabuzi F., Thaller M. C., Migliore L., Matteucci G., Italian Patent N. 102016000090701, *pending*.

New perspectives in the action of halide ions as promoter for the direct synthesis of hydrogen peroxide over palladium catalysts.

Marco Zecca[a], Chiara Dalla Valle[a], Francesco Frison[a], Paolo Centomo[a]

[a] *Department of Chemical Sciences – Università degli Studi di Padova, Padova, I-35131, Italy; marco.zecca@unipd.it*

Cl^- and Br^- ions are well known promoters for the Pd catalysts of the direct synthesis of H_2O_2 (DS) (1). This is usually attributed to site blocking which prevents dissociative chemisorption of O_2 (2) or the formation of a surface layer of PdO (3). This form of selective poisoning should lead to the decrease of the catalytic activity. We have now found that under proper conditions Br^- ions increase the selectivity of a commercial Pd/C with no appreciable drop of its activity (Figure 1). This



suggests that selective site blocking cannot be the cause of the observed effect of the promoter or the only one. As Br^- were found to be involved in Pd leaching (4) and metal phase reconstruction (5) these phenomena could provide a dynamic control of the surface coverage by atomic oxygen.

References

1. J. M. Campos-Martin, G. Blanco-Brieva, J. L. G. Fierro, *Angew. Chem. Int. Ed.***2006**, *45*, 6962–6984; C. Samanta, *Appl. Catal. Gen.***2008**, *350*, 133–149.
2. E. Ntainjua N., M. Piccinini, J. C. Pritchard, Q. He, J. K. Edwards, A. F. Carley, J. A. Moulijn, C. J. Kiely, G. J. Hutchings, *ChemCatChem* **2009**, *1*, 479–484; T. Deguchi, M. Iwamoto, *J. Phys. Chem. C***2013**, *117*, 18540–18548.
3. Q. Liu, K. K. Gath, J. C. Bauer, R. E. Schaak, J. H. Lunsford, *Catal. Lett.* **2009**, *132*, 342–348.
4. P. Centomo, C. Meneghini, S. Sterchele, A. Trapananti, G. Aquilanti, M. Zecca, *ChemCatChem***2015**, *7*, 3712.
5. P. Biasi, J.-P. Mikkola, S. Sterchele, T. Salmi, N. Gemo, A.Shchukarev, P. Centomo, M. Zecca, P. Canu, A.-R. Rautio, K. Kordàs, *AIChE J*. **2017**, *63*, 32–42.

Current efforts to make perovskite solar cells industrially viable

Federico Bella[a], *Anders Hagfeldt*[b], *Michael Grätzel*[b], *Claudio Gerbaldi*[a]

[a]*GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Torino, Italy;*
[b]*Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne, Station 3, CH1015, Lausanne, Switzerland;*
federico.bella@polito.it

Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A perovskite solar cell (PSC) is a photovoltaic device which includes a perovskite-structured compound, most commonly a hybrid organic-inorganic leadhalide-based material, as the light-harvesting active layer. These devices are cheap to produce and simple to manufacture at a laboratory level.Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to 22.1% in early 2016, making this the fastest-advancing solar technology to date.
Therefore, it is clear that – with the potential of achieving even higher efficiencies – PSCs have become commercially attractive, and a few issues should be fixed soon.
A key aspect to be taken into account in any PV technology is the operational durability of these systems in outdoor conditions. Clearly, loss of performance during operation represents a significant drawback and limitation for their commercialization. In this context, the large compositional flexibility of polymeric materials as well as their proven easy processability may be of great help in imparting improved durability to PV systems.We show that rapid light-induced free-radical polymerization at ambient temperature produces multifunctional fluorinated photopolymer coatings that confer luminescent and easy-cleaning features on the front-side of the devices, while concurrently forming a strongly hydrophobic barrier toward environmental moisture on the back contact side. The luminescent photopolymers re-emit ultraviolet light in the visible range, boosting perovskite solar cells efficiency to nearly 19% under standard illumination. Coated devices reproducibly retain their full functional performance during prolonged operation, even after a series of severe aging tests carried out for more than 6 months (1).
The industrialization of PSCs also requires the development of processes different with respect to those used in academic laboratories. For example, lab-scale PSC preparation is based on spin-coating technique, that is not transferable on a large scale. In this contribution we will also show the alternative strategies proposed by the scientific community to fabricatesolar cells components on large areas.

References

1. F. Bella, G. Griffini, J. P. Correa-Baena, G. Saracco, M. Grätzel, A. Hagfeldt, S. Turri, C. Gerbaldi, *Science* 354 (2016) 203-206.

Composition and temperature dependent Cu-speciation in Cu-SSZ-13 catalysts: an in situ XAS and FTIR study

S. Bordiga[a,b], E. Borfecchia[a,], [c] A. Martini[a], C. Negri[a], G. Berlier[a], P. Beato[c], K. A. Lomachenko[d,e], C. Lamberti[a,e], D. K. Pappas[b], M. Dyballa[b], S. Svelle[b], U. Olsbye[b]

[a]Department of Chemistry, NIS Centre and INSTM Reference Center, University of Turin, Torino, Italy;
[b]University of Oslo, Department of Chemistry, Oslo, Norway;
[c]Haldor Topsøe A/S, Lyngby, Denmark;
[d]European Synchrotron Radiation Facility, Grenoble, France;
[e]IRC "Smart Materials", Southern Federal University, Rostov-on-Don, Russia; e-mail: silvia.bordiga@unito.it

The small-pore Cu-SSZ-13 zeolite is attracting increasing attention as a versatile platform to design novel single-site catalysts for deNOx applications via NH_3-assisted Selective Catalytic Reduction (SCR) (1) and for the direct conversion of methane to methanol (MTM) (2). Cu is usually introduced into the zeolites *via* aqueous ion exchange, resulting in the formation of $[Cu(OH)]^+$ and/or Cu^{2+} counterions. Recent workspointed out that the relative abundance of $[Cu(OH)]^+$ and Cu^{2+} depends on the Cu/Al and Si/Al ratios, and proposed that only $[Cu(OH)]^+$ can be 'self-reduced' to Cu^+ sites during activation in inert atmosphere (3,4).To shed light on this aspect, which has important implications on the design and understanding of active catalysts for both SCR and MTM reactions, we prepared a large set of Cu-SSZ-13 samples with different Cu/Al and Si/Al ratios. These were characterized i*n situ* by X ray Absorption (XAS) and FTIR of adsorbed probe molecules (Figure 1), to follow Cu speciation and evolution during activation in inert conditions. Use of multivariate data-modelling allowed us to access an unprecedented level of understanding in a complex multi-component catalytic system, yielding novel insights into the birth of Cu-active sites in the cages of the SSZ-13 zeolite.

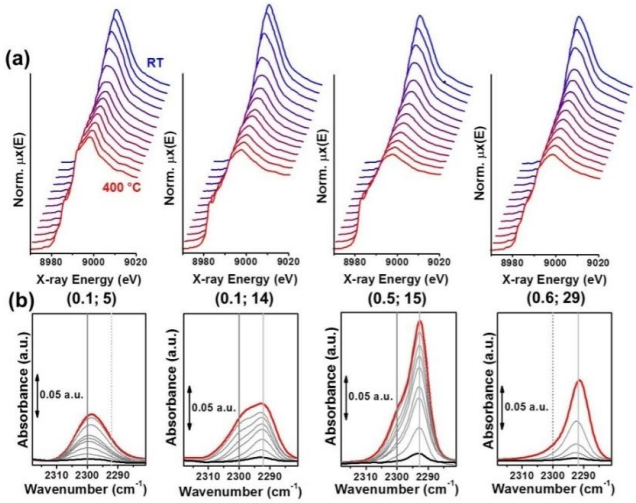


Figure 2. (a) *In situ* XANES collected on Cu-CHA at different catalyst composition (different samples are denoted with (Cu/Al; Si/Al) labels) during dehydration in He flow from 25 °C to 400 °C. (b) Low temperature normalized IR spectra of N_2 dosed at increasing equilibrium pressure on the same vacuum activated Cu-CHA catalysts.

References

1. Beale, A. M.; Gao, F.; Lezcano-Gonzalez, I.; Peden, C. H. F.; Szanyi, J. *Chem Soc Rev* **2015,***44*, 7371-7405.
2. Wulfers M.J., Teketel, S., Ipek, B., Lobo R. F., *Chem. Commun*. **2015**, *51*, 4447-4450.
3. Paolucci, C.; Parekh, A. A.; Khurana, I.; Di Iorio, J. R.; Li, H.; Caballero, J. D. A.; Shih, A. J.; Anggara, T.; Delgass, et al. *J Am Chem Soc* **2016,***138*, 6028-6048.
4. Borfecchia, E.; Lomachenko, K. A.; Giordanino, F.; Falsig, H.; Beato, P.; Soldatov, A. V.; Bordiga, S.; Lamberti, C. *Chem. Sci.***2015**, *6*, 548-563.

Conductivity and relaxation phenomena in ion conducting materials by roadband electric spectroscopy

Vito Di Noto[a,b], *Keti Vezzù*[a,b], *Enrico Negro*[a,b,c], *Federico Bertasi*[a], *Giuseppe Pace*[b,d]

[a] *Section of Chemistry for Technology, Department of Industrial Engineering, University of Padua, Via F. Marzolo 1, 35131 Padova, Italy;*
[b] *INSTM, via F. Marzolo 9, 35131 Padova, Italy;*
[c] *Centro Studi "Giorgio Levi Cases", Via F. Marzolo 9, 35131 Padova, Italy;*
[d] *CNR-ICMATE, Via F. Marzolo 1, 35131 Padova, Italy;*
vito.dinoto@unipd.it

The charge transfer mechanisms of ion conducting polymer materials (ICPMs) is of crucial importance both for fundamental research and for a host of practical applications, including primary and secondary batteries, fuel cells, dye-sensitized solar cells, supercapacitors and sensors (1). A wide variety of ICPMs has been proposed, based on: (a) different families of polymer electrolytes; (b) ionic liquids (ILs); and (c) classical ion-conducting ceramics. In these materials, the long-range charge transfer events take place owing to complex processes, which involve several possible relaxation phenomena, such as: (a) ion hopping events between ion coordination sites; (b) relaxation modes of the host matrix; and (c) polarization effects occurring at the interfaces between the different domains characterizing the materials (2-5). Broadband electrical spectroscopy (BES) is a powerful tool for the accurate investigation of the roles played by electrical relaxation events in the charge transfer processes (6). Indeed, BES allows to carefully detect the fundamental relaxations governing the long-range charge transfer mechanisms and to correlate them to the morphology of ion-conducting materials. This presentation overviews results of the application of BES in the study of the charge transfer mechanisms of a variety of ICMs, including: (a) polymer electrolytes based on alkaline and alkaline-earth ions; (b) pristine and hybrid inorganic-organic proton-conducting and anion-conducting membranes. The general phenomena and the fundamental theory underlying the interpretation of the events characterizing the electric response of the materials is also described. Finally, the models adopted for the interpretation of conductivity mechanisms are described and a unified conductivity mechanism is proposed.

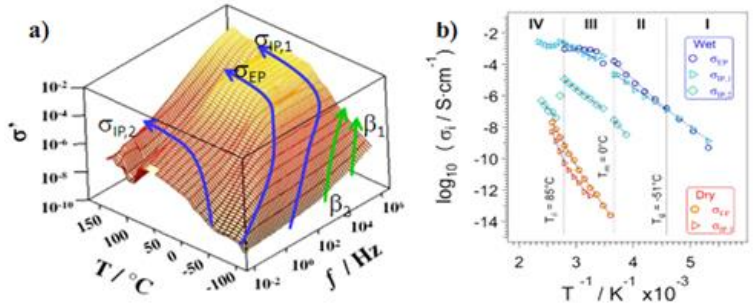


Figure 1. Three-dimensional σ' surface (a) and σ_i values vs 1/T curves of dry and wet samples in I, II, III and IV regions, delimited by thermal transitions T_g, T_m and T_δ, are fitted by Arrhenius-like behaviours (7)

References

1. Polymer Electrolytes: Fundamentals and Applications; Sequeira, C.; Santos, D., Eds.; Woodhead Publishing Limited: Oxford, 2010.
2. Di Noto, V. J. Phys. Chem. B 2000, 104, 10116.
3. Di Noto, V.; Vittadello, M. et al., Phys. Chem. B 2001, 105, 4584.
4. Di Noto, V. J. Phys. Chem. B 2002, 106, 11139.
5. Di Noto, V.; Vittadello, M. et al., J. Phys. Chem. B 2004, 108, 18832.
6. Di Noto, V.; Giffin, G. A. et al., Broadband Dielectric Spectroscopy, P. Knauth, M. L. Di Vona, Eds., John Wiley & Sons Weinheim, Germany, 2012.7. Di Noto, V.; Guinevere, G.A. et al., Phys Chem Chem Phys 2015, 17, 31125-311139.

Biosourced polymers for aqueous solar cells: a possible breakthrough towards green photovoltaic commercialization

Galliano Simone[a], Bella Federico[b], Falco Marisa[b], Barolo Claudia[a], Giordano Fabrizio[c], Boschloo Gerrit[d], Grätzel Michael[c], Hagfeldt Anders[c], Gerbaldi Claudio[b], Viscardi Guido[a]

[a] Department of Chemistry, NIS Interdepartmental Centre and INSTM Reference Centre, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 - Torino, Italy;
[b] GAME Lab, CHENERGY Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Torino, Italy;
[c] Laboratory of Photonics and Interfaces, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), Station 3, CH1015 Lausanne, Switzerland;
[d] Disciplinary Domain of Science and Technology, Chemistry, Department of Chemistry - Ångström, Physical Chemistry, Uppsala University, Box 523 SE 75120 Uppsala Sweden; simone.galliano@unito.it

In recent years, with the idea of creating efficient, safe, and low-cost DSSCs, the research moved the attention towards alternative solvent-based electrolytes. Above all, DSSCs with water-based electrolytes have been proposed as one of the possible solution providing reduced costs, non-flammability and environmental compatibility (1). Recently we demonstrated that stability issues can be properly addressed by choosing sensitizers with appropriate molecular structure (2). Moreover, the possibility of gelling the liquid solvent into a polymeric matrix can reduce the electrolyte leakage outside the device, increasing the long-term stability, without limiting the overall photovoltaic performances.
In this contribution, the investigation on a series of iodine and cobalt-based 100% aqueous electrolytes is presented. Thanks to our previous experience (3) and to a multivariate approach (Design of Experiment), the effects of the change in redox mediator concentrations and in photoanode preparation on DSSCs performances have been evaluated.
Finally, the gelation of the best aqueous electrolytes with low-cost, bio-derived polymers has been performed (4). Photovoltaic performances and stabilities will be discussed by comparing liquid and gel electrolytes. In lab-scale solar cells interesting photovoltaic efficiencies close to 4.5% were achieved.

References

1. F. Bella, C. Gerbaldi, C. Barolo and M. Grätzel, Chem. Soc. Rev., 2015, 44, 3431-3473.
2. S. Galliano, F. Bella, C. Gerbaldi, M. Falco, G. Viscardi, M. Grätzel and C. Barolo, Energy Technol., 2017, 5, 300-311.
3. F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel and C. Gerbaldi, Chem. Sci., 2016, 7, 4880-4890.
4. F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel and C. Gerbaldi, Green Chem, 2017, 19, 1043-1051.

Development of N-doped TiO_2 catalyst for the photocatalytic treatment of wastewater in presence of visible light irradiation

Olga Sacco[a], *Vincenzo Vaiano*[b], *Wanda Navarra*[a], *Christophe Daniel*[a,c], *Vincenzo Venditto*[a,c]

[a]*University of Salerno, Department of Chemistry and Biology, A. Zambelli, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy,*
[b]*University of Salerno, Department of Industrial Engineering, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy,*
[c]*INSTM Research Unit, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA) Italy*

Traditional methods for wastewater treatment are usually based on physical and biological processes but unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In this way heterogeneous photocatalysis may become an interesting water treatment technology to remove organic pollutants. The most common used photocatalyst is TiO_2. It is able to oxidize a wide range of toxic organic compounds into harmless compounds such as CO_2 and H_2O. Due to the value of TiO_2 band-gap energy, about 3.2 eV, it is effective only under irradiation of UV light. This is a technological limitation when aiming at implementation of large scale sustainable "green" technologies with renewable energy sources such as solar light. The main research objectives for the application of TiO_2 as a photocatalyst is the increase the photocatalytic performances of TiO_2 through the doping of its crystalline structure with non-metal ions (nitrogen) that reduce the band-gap making possible the absorption of the visible light. The results obtained from our research activity evidenced that the doping of TiO_2 with nitrogen (N-TiO_2) has led to an enhanced photocatalytic activity in presence of visible light irradiation. The optimized formulation of N-TiO_2 has shown very effective in the removal of organic dyes, such as methylene blue and methyl orange (1), antibiotics such as spyramicin (2) and in the inactivation of E.coli (3). However, one of the most important drawbacks of photocatalytic process is that photocatalysts are often used in slurry reactors. The limitation of slurry process is that the photocatalyst in powder form must be separated from the purified water after the treatment, and the cost of this separation stage may even invalidate economically this technique. With the aim to overcome this technical limitation, an innovative structured catalyst, in which N-TiO_2 is dispersed in transparent syndiotactic polystyrene monolithic aerogels (s-PS) has been developed (4). In particular, s-PS aerogels, due to their high specific surface area, present the possibility to disperse the catalysts in powder form, overcoming the aggregation phenomena that commonly happen when the catalyst is suspended in water solutions. These features allow not only to have a structured catalyst, but also to increase the photocatalytic activity of the N-TiO_2 under visible light in comparison with the powder sample dispersed in solution (4).

References

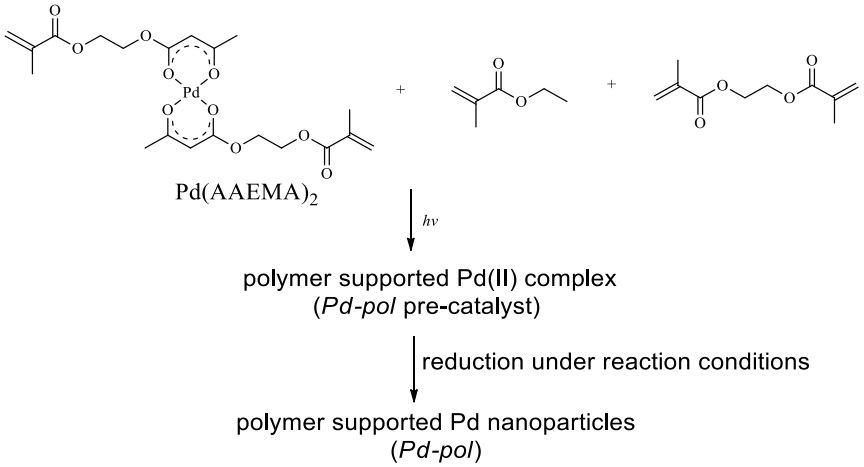
1. Sacco, O., Stoller, M., Vaiano, V., Ciambelli, P., Chianese, A., and Sannino, D. (2012). "Photocatalytic degradation of organic dyes under visible light on N-doped TiO_2 photocatalysts." International Journal of Photoenergy, Volume 2012, Article ID 626759, 8 pages, doi:10.1155/2012/626759.
2. Vaiano, V., Sacco, O., Sannino, D., and Ciambelli, P. (2014). "Photocatalytic removal of spiramycin from wastewater under visible light with N-doped TiO_2 photocatalysts." Chemical Engineering Journal, http://dx.doi.org/10.1016/j.cej.2014.02.071.
3. Rizzo, L., Sannino, D., Vaiano, V., Sacco, O., Scarpa, A., and Pietrogiacomi, D. (2014). "Effect of solar simulated N-doped TiO_2 photocatalysis on the inactivation and antibiotic resistance of an E. coli strain in biologically treated urban wastewater." Applied Catalysis B: Environmental, 144, 369-378.
4. Vaiano, V., Sacco, O., Sannino, D., Ciambelli, P., Longo, S., Venditto, V., and Guerra, G. (2014). "N-doped TiO_2/s-PS aerogels for photocatalytic degradation of organic dyes in wastewater under visible light irradiation." Journal of Chemical Technology and Biotechnology, 89(8), 1175-1181.

Polymer supported palladium nanoparticles as catalyst for organic reactions in water

Maria Michela Dell'Anna[a], *Matilda Mali*[a], *Giuseppe Romanazzi*[a], *Antonino Rizzuti*[a], *Cristina Leonelli*[b], *Piero Mastrorilli*[a]

[a]*DICATECh, Politecnico di Bari, via Orabona, 4, 70125 Bari, Italy;*
[b]*DEF, Università di Modena e Reggio Emilia, via Vivarelli, 10, 41125 Modena, Italy;*
mariamichela.dellanna@poliba.it

An insoluble palladium catalyst (*Pd-pol*) was obtained by copolymerization of the metal containing monomer $Pd(AAEMA)_2$ [$AAEMA^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with ethyl methacrylate (co-monomer)and ethylene glycol dimethacrylate (cross-linker), followed by *in situ* reduction of Pd(II) to Pd(0), to give polymer stabilized metal nanoparticles (Scheme 1). The good swellability in water exhibited by *Pd-pol* rendered it an ideal potential catalyst for reactions carried out in a *green* solvent, such as water, since the migration of the reagents to the active sites would not be hampered by the solid support.



Scheme 1: synthesis of *Pd-pol*

With the aim to develop innovative catalytic processes that enable chemical transformations to be performed under mild and sustainable conditions with high efficiency, we decided to evaluate the catalytic activity of *Pd-pol* for several important organic reactions using water as solvent (1). *Pd-pol* resulted highly active and selective in catalyzing: the Suzuki-Miyaura coupling between aryl bromides or activated aryl chlorides and phenylboronic acid (2); the oxidation of benzyl alcohols to aldehydes (3); the reduction of quinolines (4,5) and nitroarenes (6) by H_2 or $NaBH_4$.
Pd-pol was recyclable for several consecutive runs (for example, at least twelve times in the nitroarene reduction). TEM analyses carried out on the catalyst showed that the active species were supported palladium nanoparticles having a mean size of 4 nm, which did not aggregate with the recycles.

References

1. P. Mastrorilli, M.M. Dell'Anna, A. Rizzuti, M. Mali, M. Zapparoli, C. Leonelli, Molecules, 20 (2015) 18661-18684.
2. M.M. Dell'Anna, M. Mali, P. Mastrorilli, A. Rizzuti, C. Ponzoni, C. Leonelli, J. Mol. Catal. A: Chem. 366 (2013) 186–194.
3. M.M. Dell'Anna, M. Mali, P. Mastrorilli, P. Cotugno, A. Monopoli, J. Mol. Catal. A: Chem. 386 (2014) 114–119.
4. M.M. Dell'Anna, V.F. Capodiferro, M. Mali, D. Manno, P. Cotugno, A. Monopoli, P. Mastrorilli, Appl. Catal. A: Gen. 481 (2014) 89–95.
5. M.M. Dell'Anna, G. Romanazzi, S. Intini, A. Rizzuti, C. Leonelli, A. F. Piccinni, P. Mastrorilli, J. Mol. Catal. A: Chem. 402 (2015) 83–91.
6. M.M. Dell'Anna, S. Intini, G. Romanazzi, A. Rizzuti, C. Leonelli, F. Piccinni, P.Mastrorilli, J. Mol. Catal. A: Chem. 395 (2014) 307–314.

Bromobutyl rubber synthesis: influence of the reaction temperature on product distribution

Rosa Vitiello[a], Rosa Turco[a], Vincenzo Russo[a], Martino Di Serio[a], Riccardo Tesser[a]

[a] University of Naples "Federico II" Department of Chemical Sciences, Via Cinthia (80126) Naples (Italy); rosa.vitiello@unina.it

Bromobutyl rubber is obtained by reacting butyl rubber with bromine. It has increased cure reactivity, higher compatibility with unsaturated polymers and enhanced adhesion compared to butyl rubber and higher thermal stability (1).
The bromobutyl rubbers are primarily used for the tires production, to produce tire inner liners and tire sidewalls, and are also used for tire treads. It is also suitable for pharmaceutical stoppers and rubber articles needing good resistance to chemicals, weathering, and ozone, such as tank linings, conveyor belts, and protective clothing. Vulcanizes have excellent resistance to weathering, ozone, and hot air; very good resistance to acidic and basic chemicals; very low permeability to gases and liquids; and good rheological properties (1).
Bromobutyl rubber is prepared by reacting bromine with a butyl rubber dissolved in n-hexane, at about 50°C (2). The reaction occurs involving the unsaturated isoprene units dispersed in the polymer. The bromination reaction proceeds through a double bond shift and the formation of an exo-methylene allylic bromide.However, some allylic rearrangements and double bonds migration can follow. As a matter of fact,four different structures have been individuated in bromobutyl rubbers (BIIR) (3).
For example, HBr formed during bromination can react in a successive step by addition to the double bonds giving place to organic bromine but this structure is not active for the industrial purpose. It is possible to obtain also endo brominated structure but these structures are not important for the industrial purpose because they do not contribute to form the crosslinked networks.
In this work the screening of the operative conditions was performed in order to obtain the highest percentage of exo-methylene allylic bromide structure.

References

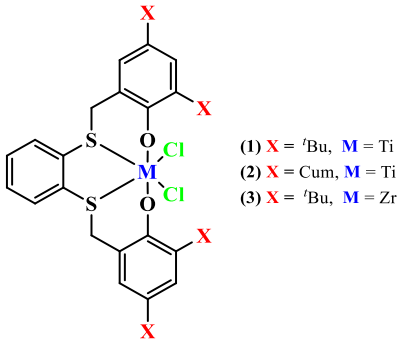
1. R. Vitiello, R. Tesser, R. Turco, E. Santacesaria, G. Compagnone, and M. Di Serio, A Critical Review on Analytical Methods and Characterization of Butyl and Bromobutyl Rubber. International Journal Of Polymer Analysis And Characterization. http://dx.doi.org/10.1080/1023666X.2017.1297887.
2. W. Wang,H. K. Zou, G. W. Chu, Z. Weng, Chen, J. F. 2014. Bromination of butyl rubber in rotating packed bed reactor. Chem. Eng. J. 240: 503-508.
3. W. Wang, H. K. Zou, G. W. Chu,Y. Xiang, H. Peng, Chen, J. 2014. Effects of assistant solvents and mixing intensity on the bromination process of butyl rubber. Chin. J. Chem. Eng., 22, 4: 398-404.

Stereorigid OSSO-type group 4 metal complexes in the polymerization of olefins and polar monomers

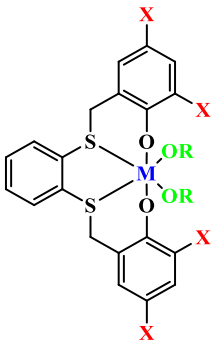
Rosita Lapenta[a],*Antonio Buonerbaa, Assunta De Nisi*[b], *Magda Monari*[b], *Alfonso Grassia, StefanoMilionea, Carmine Capacchione*[a]

[a]*Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 132 Fisciano, I-84084 Salerno, Italy;* [b]*Dipartimento di Chimica G. Ciamician, Alma Mater Studiorum, Università di Bologna, via Selmi 2, Bologna, Italy; rlapenta@unisa.it*

Among the post-metallocene catalysts active in the polymerization of unsaturated monomers, an interesting class of compounds is represented by group 4 complexes bearing thioetherphenolatechelating ligands, the (OSSO)-typeligands. These ligands are generally formed by two phenoxide groups linked to two donor sulfur atoms in the ortho or benzyl positions using nucleophilic substitution between the suitable phenols and dithiol. The resulting linear tetradentate OSSO ligands wrap around the group 4 metal center producing octahedral coordination geometries with special electronic and steric properties. The corresponding group IV metal complexes are known for the high performance in the α-olefin polymerization, yieldingstereoregular and high molecular weight polymers(1).Moreover, the alkoxide derivative of the [OSSO]-type group IV complexes are powerful initiators in the ring opening polymerization (ROP) of cyclic esters to obtained biodegradable and biocompatible materials, extremely interesting in biomedical fields thanks to the low toxicity of the catalytic ashes(2).In an effort tofurther examine the structure−activity relationships affectingthe reactivity and the stereoselectivity of this class of compounds, wehave prepared and structurally characterized anew series of group 4 metal complexessupported by*o*-phenylene-bridged bis(phenolato) ligands with general formula {$OSSO_X$}$M(Cl)_2$(X = tBu, M = Ti (**1**); X = cumyl, M = Ti, (**2**); X = tBu, M = Zr (**3**)) and {$OSSO_X$}$M(OR)_2$(X = tBu, M = Ti, R = iPr (**4**); X = R = tBu, M =Zr (**5**); X = cumyl, M = Zr, R = tBu (**6**); X= cumyl, M = Hf, R = tBu (**7**)).Compound**1-3**,combined with MAO, promote the reaction of ethylene and propeneyielding the corresponding polymers containing unsaturated end groups produced via aβ-hydrogen elimination reaction. Differently alkoxide derivatives **4-7** are active catalyst in the ring opening polymerization of *rac*-lactide.In the presence of exogenous alcohol, narrow molecular weight distributions and molecular weights of the resulting PLAs proportional to the equivalents of added isopropanol suggest that adequate conditions for effective “immortal” polymerizations are achieved (3).



(1) X = ^{t}Bu, M = Ti
(2) X = Cum, M = Ti
(3) X = ^{t}Bu, M = Zr



(4) X = ^{t}Bu, M = Ti, R = ^{i}Pr
(5) X = ^{t}Bu, M = Zr, R = ^{t}Bu
(6) X = Cum, M = Zr, R = ^{t}Bu
(7) X = ^{t}Bu, M = Hf, R = ^{t}Bu

References

1. Nakata, N.; Toda, T.; Ishii, A. *Polym. Chem*. **201**1, *2*, 1597−1610.
2. Sauer, A.; Kapelski, A.; Fliedel, C.; Dagorne, S.; Kol, M.; Okuda, J. *Dalton Trans.*, **2013**,*42*, 9007-9023.
3. Lapenta, R.; Buonerba, A.; De Nisi, A.; Monari, M.; Grassi, A.; Milione, S.; Capacchione, C. *Inorg. Chem.***2017**, *56*, 3447–3458.

Smart formulations for cosmetic industrial applications

Elena Ghedini[a], *Michela Signoretto*[a], *Alessia Costantin*[b], *Alessandria Semenzato*[b],*Giuseppina Cerrato*[c]

[a] *Dip. di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Consorzio INSTM-UR di Venezia, Via Torino 155, 30172 Mestre Venezia, Italia;*
[b]*UNIRED S.r.l., Via Niccolò Tommaseo 69, 35131 Padova, Italia;*
[c]*Dip. di Chimica & Centro Interdipartimentale NIS - Università degli Studi di Torino & Consorzio INSTM-UR di Torino, Via P. Giuria 7, 10125 Torino, Italia; e-mail: gelena@unive.it*

Globally the cosmetic industry is a leading sector in the economy and the European cosmetics and personal care market is the largest in the world.
The largest national markets for cosmetics and personal care products within Europe are Germany (€13 billion), United Kingdom (€12.5 billion), France (€11.3 billion), and Italy (€9.7 billion)[1].The cosmetics industry is a science-driven and highly innovative sector which makes large investments in research and development in order to obtain increasingly performing and sustainable products.
The goal of this project was the formulation of innovative products for use in cosmetics through the development of a sustainable protocol aimed to the synthesis of high performant products but at the same time sustainable, in the maximum respect for the environment and for end users.
The attention was focused, in particular, on the development of gel for the body care (products to prevent skin aging, or designed to correct skin defects, such as blemishes and scars) choosing natural components whose efficiency will be maximized with the use of advanced technologies. For this purpose was used the Drug Delivery Systems technology (DDS, controlled release of an active molecule) already known and widely used in the pharmaceutical field but not effectively exploited in cosmetics. These systems help to optimize dosing, bioavailability and efficacy of active pharmaceutical ingredients already known and administered by traditional route[2,3]. This approach, when used in cosmetics allows to maximize the effectiveness of the active ingredients, overcoming the intrinsic limitations of the same (for example poor bioavailability) making the final products efficient and consequently more attractive to the consumer.
The gel was formulated by a sustainable "one-pot" sol-gel approach. A hybrid organic-inorganic material made of silica, chitosan, a polysaccharide derived from agri-food waste, and fatty acid such as azelaic and glycolic acids was used as matrix. Caffeine (with antioxidant properties) was selected as active molecules. The products features were analyzed in depth by FT-IR, Raman spectroscopy,by rheological tests and by microscopy analyses. The evaluation of the drug delivery properties of the gels was performed in vitro and ex vivo by using a vertical Franz diffusion cell. We have studied synthetic membranes (PVDF or Strat-M membranes formed from polyolefins in stratified polyether sulfone) and biologically derived membranes (ex vivo, for example pork membranes) in order to draw up a reproducible and reliable protocol for the release test capable of reproducing at best the real conditions of use of the formulated gel.

References

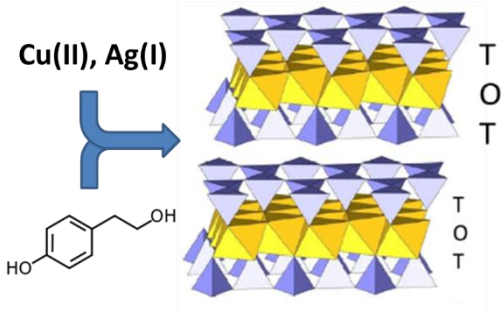
1. Cosmetics Europe, https://www.cosmeticseurope.eu/cosmetics-industry
2. E. Ghedini, M. Signoretto, V. Nichele, G. Cerrato, Agents for the Synthesis of TiO2-Based Drug-Delivery Systems"
1. Chem. Eur. J. 18 (2012) 10653-10660.
2. M. Signoretto, E. Ghedini, V. Nichele, F. Pinna, D. Casotti, G. Cruciani, V. Aina, G.Martra, G.A. Cerrato, Formulation of Innovative Hybrid Chitosan/TiO2 and Chitosan/SiO2 based Drug Delivery Systems,
3. Multi-Volume SET (I-V) "Therapeutic Nanostructures, Volume 2: Drug Delivery", Editor: Alexandru Mihai Grumezescu, Bucharest, (2016), (Articolo su libro).

Inorganically and organically modified mineral clays: a sustainable approach in the control of the olive tree fly pest, *Bactrocera oleae*

Matteo Guidotti[a], *Rinaldo Psaro*[a], *Elisabetta Gargani*[b], *Alessandro Caselli*[a,c], *Enrico L. Appiani*[c], *C. Cattaneo*[d], *Roberto Rappuoli*[d]

[a] *CNR-Istituto di Scienze e Tecnologie Molecolari, Milano;*
[b]*CREA–ABPDC, Centro di Ricerca per l'Agrobiologia e la Pedologia (Entomologia) Difesa e Certificazione, Firenze;* [c] *Dipartimento di Chimica, Università degli Studi di Milano, Milano;*
[d]*Azienda Agricola Podere Forte, Castiglione d'Orcia (SI)*
m.guidotti@istm.cnr.it

The most relevant phytophagous insect associated with olive tree plantations crops throughout the Mediterranean area is *Bactrocera oleae*, the olive tree fly. Innovative and environmentally-friendly methods for the mitigation of such pest have been attracting an ever-increasing attention, especially after 2014, when the whole Italian olive oil production suffered from dramatic losses. Novel prevention strategies should meet four main criteria: toxicologic safety, environmental selectivity and compatibility, pest-control efficiency and economic sustainability. In this aim, two series of solids showing a detrimental effect on the life cycle of *Bactrocera oleae* have been designed and prepared, *i.e.* montmorillonite-based clays from mineral origin containing: i) Group 11 transition metal cationic species, such as Cu(II) and Ag(I) or ii) polyphenolic organic compounds derived from olive mill waste waters. The bioactive solid materials have been prepared either by ionic exchange from aqueous solutions of sulfate or nitrate metal precursors at various concentrations or by impregnation of the polyphenol-containing effluents onto the clay support, respectively (Scheme 1). In the case of metal-based solids, by optimising the ion-exchange procedure, a fully adequate bioactive metal content was reached for practical purposes, although reducing by more than 80% the use of precursor salts with respect to the current state of the art (1). These materials contain approx. 5 wt.% of active metal and possess acid sites, which not only, when dispersed on the fruit surface, inhibit the egg-laying activity of flies into the olives, but also catalytically-active metal cation sites with enhanced biocide effect against parasites of several crops (2). In polyphenol-modified solids, on the other hand, amounts of organics in the range of 0.9-2.6 wt.% can be deposited. Thanks to the immobilisation within the interlayer spaces of the clay, lower concentrations of bioactive species may be applied onto the olive tree, thus reducing the potential undesired dispersal of the active molecules into the environment. In order to evaluate the performance of the most promising solids in open-field tests, two sets of experimental campaigns have been carried out on olive tree orchards in Southern Tuscany, in summer 2015 and 2016.



Scheme 1: inorganic or organically modified clays

Preliminary promising results have been obtained with Cu(II) species and with aqueous-phase olive mill wastewaters deposited onto bentonite-like montmorillonite clays, in terms of reduction of both fly infestation and damages on the olive fruit. These materials have indeed proved to be easily prepared, cost effective, environmentally friendly, stable to rainwater leaching, toxicologically safe and led to a remarkable diminution in the use of bioactive species for on-field applications.

CNR-ISTM and CREA-ABPDC gratefully acknowledge Podere Forte and Laviosa Chimica Mineraria.

References

1. Baker, H. Desalination, 244 (2009) 48. 2. Belcari, A., Bobbio, E., Informatore Fitopatologico, 12 (1999) 52.

Modeling approach for applied research: the case-study of PLA synthesis by ring-opening polymerization of lactide

Mirco Nodari[a], *Aldo Longo*[a], *Dino Ferri*[a], *Andrea Perolo*[a]

[a,] *Versalis S.p.A., Centro Ricerche C. Buonerba, via G. Taliercio n°14, 46100, Mantova; mirco.nodari@versalis.eni.com*

The use of predictive models is a key tool for the comprehension and the development of chemical processes, especially for very complex systems like those in the field of materials science. Polymer Reaction Engineering (PRE) is a multidisciplinary approach that can be conveniently employed for the study of (novel) polymerization processes: in doing so, rationalization of the experimental trials, deeper understanding of the chemistry involved and certain predictive skill towards the process can be achieved. Such a result has useful implications also in terms of ability to control the physico-chemical properties of the product and process safety.

Many chemical companies use predictive models and Versalis, among these, adopted such tools in support of consolidated production processes as well as for the most recent R&D activities. Here the work done at the Versalis Research Centre of Mantova on the synthesis of PLA by Ring-Opening Polymerization (ROP) of lactide is presented. The production of PLA can be considered one of the most important processes for the synthesis of bio-based polymers to reach the commercial scale. Based on the kinetic scheme by Yu et al.[1], the process has been modeled for different reactor configurations by means of implementation and calculation with MathWorks® MATLAB® software, applying the method of moments. The results of the simulations have been compared with those obtained from a set of experimental trials, with the aim of studying the dependence of the polymeric mixtures properties on the reaction parameters (temperature, feed composition, catalytic system composition, reaction time, impurities) and validatingthe predictivity of the model in terms of conversion to polymer and molecular weight distributions.

In addition to the polymerization kinetics, some experiments were carried out in order to study transport phenomena of lactide/PLA mixtures, such as heat transfer and rheological properties[2], and their dependence on polymer content and molecular weight distribution.

In conclusion, provided that the models here discussed can be further developed in order to cover additional features like scale factors, fluid dynamics and non-ideality of real systems, the use of such an integrated approach has led to a deeper understanding of the process, giving key information and guidelines for a potential design on an industrial scale.

References

1. Yu Y., Storti G., Morbidelli M., “Kinetics of Ring-Opening Polymerization of L,L-Lactide”, Ind. Eng. Chem. Res. 2011, 50, 7927–7940.
2. Ferri D., Perolo A., Nodari M., “Cross-WLF parameters to predict rheological properties of polylactic acid”, 25th volume of the Annual Transactions of the Nordic Rheology Society (ATNRS), 2017.

Chemical research in the field of galvanic industries and fashion accessory

M. Innocenti[a], *M. Passaponti*[a], *E. Salvietti*[a], *S. Martinuzzi*[a], *E. Piciollo*[b], *S. Mariottini*[c], *L. Rosi*[a], *S. Caporali*[d], *W. Giurlani*[a], *F. Di Benedetto*[e].

[a]*Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy.*
[b]*LEM s.r.l. Socio Unico, via Valiani 55, 52021 Levane, Arezzo, Italy.*
[c] *E.s.a. Di Mariottini Ivo, via Calamandrei Pietro 105, 52100 Arezzo, Italy.*
[d]*Università degli Studi di Firenze, Dipartimento di Ingegneria Industriale (DIEF), S. Marta 3, 50134, Firenze, Italy.*
[e]*Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4,50121, Firenze (Italy); minnocenti@unifi.it*

The fashion market is by its very nature and requires continuous and innovative changes, but the galvanic industry has slower adaptation and response times.Galvanics are based on traditional knowledge that is sedimented over time, which is unlikely to be open to innovation and innovation.
As for the state of the art of technology, innovation lies in the goal of creating a modular and flexible galvanic that allows the study and creation of new production processes by varying the succession of layers of metals or alloys that normally settle in an attempt to increase the qualitative properties of the final accessory.In addition, in Galvanic Industries the problems associated with the analytical control of galvanic baths and the evaluation of the thicknesses of each single layer deposited that makes up the fashion accessory are the most felt demands of the companies.
In this presentation we show the results of an interesting collaboration born and consolidated in recent years between the Applied Electrochemistry Laboratory of the Department of Chemistry, University of Florence, and many companies related to the "fashion" world. The ability to know the demands of those who produce (galvanic industries) and who packs (YSL, Gucci, Prada etc) has made it possible to adapt their research to the industrial specificities of the territory by trying to produce products with low environmental impact and low energy demand.

Manipulating the arrangement of arrays of nanoparticles on solid supports by using self-assembled block copolymers templates

Anna Malafronte[a], *Claudio De Rosa*[a], *Finizia Auriemma*[a], *Carmen Sasso*[a,b]

[a] *Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy;*
[b] *ENEA Italian National Agency for New Technologies, Energy and Sustainable Development, SSPT-PROMAS-NANO Department, P.zza E. Fermi 1, I-80055 Portici, Napoli, Italy; anna.malafronte@unina.it*

Nanoparticles (NPs) exhibit a number of unique optical, electronic, and catalytic characteristics compared to those of bulk materials because of the small-size effect and extremelylarge specific surface area (1). Since the majority of unique properties of NPs is highly microstructure-dependent, forming arrays of NPs on solid supports with precisecontrol of the dimensions, spacingand morphology is animportant issuefor most scientific and technical applications.
We report the fabrication of two-dimensional arrays of different NPs (Pd, PdO, ZnO) on solid supports (glass, silicon, indium thin oxide (ITO)-coated slides) by exploiting the self-assembly of diblock copolymers (BCPs) to control the positioning of NPs, their characteristic sizes and lateral spacing.
BCPs consist of covalently linked distinct macromolecules that tend to segregate into different nanodomains due to their mutual repulsion, resulting in the spontaneous formation of periodic nanostructures by self-assembly (2).We have used nanodomains of self-assembled BCPs as hosts for sequestering NPs, producing nanocomposites with different morphologies (cylindrical andlamellar). The sizes and shapes of the arrays of NPs have been conveniently tuned by changing the molecular mass and compositions of the BCPs.
In particular, in the first part we present a systematic investigation of nanocomposite thin films based on polystyrene-*block*-poly(ethylene oxide) copolymers (PS-PEO), characterized by selective inclusion of palladium (Pd) species (Pd-acetate and Pd NPs) in the PEO domains (3). Cylindrical phase-separatedPS-PEO copolymers of different total molecular mass have been used to tune the characteristic sizes (diameter and lateral spacing) of the included Pd species. Arrays of palladium oxide (PdO) NPs, characterized by different particles diameters and gap distances, mirroring the pattern and the characteristic nanodimensions of the parent BCPs used as template, have been also obtained by treatment of the nanocomposites at elevated temperatures in air.
In the second part, the morphology and the electrical properties of hybrid nanocomposites characterized by the dispersion of ZnO NPs, a *n*-type semiconductor, within an organic nanostructured matrix of polystyrene-*b*-poly(methyl methacrylate) (PS-PMMA) copolymer are presented. A selective inclusion of NPs into the lamellar PS nanodomains of the BCP matrix has been achieved by synthetizing*ad hoc*organic-capped ZnO NPs and by thermal annealing the nanocomposites ZnO NPs/PS-PMMA. The study of the electrical proprieties of the nanocomposite confirms the key role of the nanostructured BCP for the obtainment of good conductive properties and make the BCP-based approach a promising strategy for the fabrication of materials for photovoltaic applications.

References

1. Altavilla, C.; Ciliberto, E. Inorganic Nanoparticles: Synthesis, Applications, and Perspectives; CRC Press: Boca Raton, FL, 2011.
2. Hamley, I. W. The Physics of Block Copolymers; Oxford University Press: Oxford, 1998.
3. De Rosa, C.; Auriemma, F.; Malafronte, A.; Di Girolamo, R.; Lazzari, M.; Nieto-Suarez, M.; Hermida-Merino, D.; Hamley, I. W.; Portale, G. *J. Phys. Chem. B* 2016, *120*, 6829.

New sustainable technology to recover returned concrete

Giorgio Ferrari

Mapei S.p.A., Via Cafiero 22, 20158, Milano (Italy); g.ferrari@mapei.it

Concrete is the second most used material in the world, after water. More than 10,000 million cubic meters are globally produced every year, with the consumption of more than 19,000 million Tonnes of natural aggregates (coarse aggregates and sand) (1, 2). For different reasons, about 300 million cubic meters of concrete (3 per cent of the global production) are not placed at the jobsite and are returned to the ready-mixed production plant where, in most cases, are disposed to landfill as waste material. Recently, a new technology to treat returned concrete has been developed: one cubic meter of returned concrete is treated with non-dangerous additives and transformed, in few minutes, into 2.3 Tonnes of aggregates, without any waste production (3). The new aggregates can be used to produce new concrete materials, with excellent mechanical performance and environmental compatibility. The new method has many advantages because it allows to save virgin aggregates and to reduce the natural resource depletion. Furthermore, returned concrete is 100% recovered and no waste is produced, completely eliminating landfill disposal. For these reasons, the new technology has a positive effect on the environmental impact of returned concrete, with hundred-fold reductions of the main parameters characterizing the environment footprinting. Furthermore, the new technology allows a reduction of the costs for both waste disposal and aggregates supplying, representing an excellent example circular economy.

Figure 1. Example of newly formed aggregate from returned concrete

References

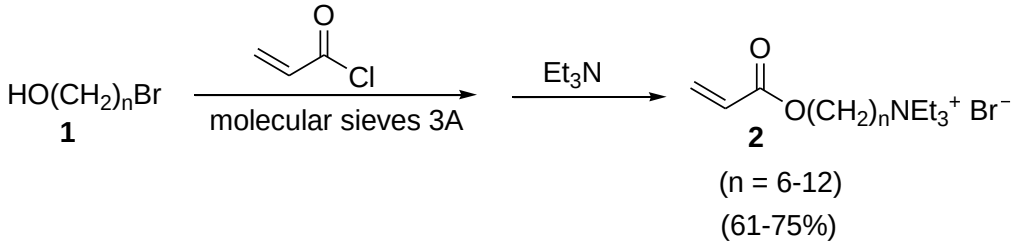
1. Obla, K., Kim, H. and Lobo, C., “Crushed returned concrete as aggregate for new concrete – Final report”, RMC Research & Education Foundation, 2007.
2. Sato, Y., Oyamada, T. and Hanehara, S., “Applicability of sewage sludge ash (SSA) for paving material: A study on using SSA as filler for asphalt mixture and base course material”, Proceedings of the Third International Conference on Sustainable Construction Materials and Technologies, Kyoto, Japan, 2013.
3. Ferrari, G., Brocchi, A., Cella, F., Dalconi, M.C. and Longhi, F., “Aggregates from residual concrete”, Proc. twelfth international conferenceon recent advances in concrete technology and sustainability issues, Am. Concr. Inst., SP-289, Prague 2012, pp. 113-127.

Acryloxyalkyltriethylammonium bromides (AATEABs): useful starting materials for the preparation of polymeric membrane coatings with anti-biofouling properties

Raffaella Mancuso[a], *Roberta Amuso*[b], *Biagio Armentano*[c], *Anna R. Cappello*[c], *Francesco Galiano*[b], *Alberto Figoli*[b], *Jan Hoinkis*[d] *and Bartolo Gabriele*[a]

[a]*Laboratory of Industrial and Synthetic Organic Chemistry (LISOC), Department of Chemistry and Chemical Technology, University of Calabria, Via Pietro Bucci, 12/C, 87036 Arcavacata di Rende (CS), Italy;*
[b]*Institute on Membrane Technology, National Research Council (ITM-CNR), Via Pietro Bucci 17/C, 87036 Arcavacata di Rende (CS), Italy;*
[c]*Department of Pharmacy and Health and Nutritional Sciences, University of Calabria, 87036 Arcavacata di Rende (CS), Italy;*
[d]*Institute of Applied Research, Karlsruhe University of Applied Sciences, Moltkestreet 30, 76133 Karlsruhe, Germany;*
raffaella.mancuso@unical.it

Polymerizable quaternary ammonium salts (PQASs) are important starting materials for the development of innovative polymers with antimicrobial activity. We report herean efficient synthetic approach for the preparation of a particularly important class of PQASs, that are, acryloxyalkyltriethylammonium bromides (AATEABs)**2**, which may find application for the development of antimicrobial coatings for commercial membranes with antifouling and anti-biofouling properties. The synthetic approach for the production of AATEABs**2** bearing an alkyl chain of 6, 9, 11, and 12 carbon atoms (Scheme 1) is based on a simple two-step procedure from commercially available substrates**1**, entirely carried out under air and without any need for chromatographic purification.



Scheme 1

All the newly synthesized AATEABs were tested for their antimicrobial activity, and the results evidenced that AATEABs bearing an alkyl chain of 11 and 12 carbon atoms (AUTEAB and ADTEAB, respectively) possessed significant activity against Gram +ve bacteria and yeast strains. Accordingly, these derivatives are excellent candidates for the industrial development of novel antimicrobial polymers and materials. In particular, we have efficiently employed AUTEAB and ADTEABfor the development of novel polymeric coatings for the surface functionalization of commercial membranes. The novel nanostructured membranes thus obtained are characterized by significant anti-fouling and anti-biofouling properties, and can be efficiently employed in industrial wastewater treatment.

Acknowledgment
The work performed has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 689427 for the project VicInAqua.

Novel ion-exchange catalysts for the esterification of vegetable oil solutions of fatty acids with methanol

Paolo Centomo[a], Chiara Dalla Valle[a], Federico Rastrelli[a], Sandro Campestrini[a], Marco Zecca[a]

[a]Department of Chemical Sciences – Università degli Studi di Padova, Padova, I-35131, Italy;
e-mail: paolo.centomo@unipd.it

The acid catalyzed esterification (ACE) of fatty acids (FA) is a key process to upgrade oils with FA contents higher than 5% and make them available as raw materials for the production of biodiesel by the base catalyzed trans-esterification of natural triglycerides.
We show herein that a novel mesoporous form of sulfonated poly-divinylbenzene (pDVB_s) prepared by polymerization of DVB under high dilution condition (1) outperforms the conventional gel-type and macroreticular ion-exchange catalysts (IECs), and that its catalytic sites are almost as effective as those of p-toluenesulfonic acid in the model esterification of stearic acid (SA) with a large excess of methanol (2). Conventional gel-type IECs rely on full swelling, ensured by the relatively high amount of alcohol, to make their sulfonic groups accessible and achieve the highest activity (3). The activity of macroreticular IECs, which possess a permanent pore system, is less dependent on swelling, but not as high as that of gel-type catalyst under optimal conditions. In this respect, the mesoporous pDVB employed in this work is featured by the unusual combination of relatively large pore diameters, high pore volumes and permanent specific surface areas much higher than in macroreticular resins (4). As the consequence the surface of permanent pores can accomodate a large proportion of sulfuric groups, which are almost as efficient as those of a homogeneous catalyst and ensure a high catalytic activity.
The polar nature of the sulfuric groups make the micro-environment around he catalytic sites of IECs hydrophilic hence relatively little compatible with FA. The hydrophobic character of mesoporous pDVB was therefore enhanced by the introduction of fluorinated ponytails (C4F7O). This is expected to improve the catalytic performance of the IEC due to the assisted absorption of SA and the expulsion of water, a by-product of the reaction (5). For comparison we introduced the same kind of ponytails in a gel-type IEC, too. A measurable, albeit small, the improvement of the catalytic activity was observed only for the modified gel-type catalyst. For modified pDVB_s the effect of the functionalization was observed when the esterification was carried out in the presence of water (10% w, with respect methanol). Under these conditions the final conversions of SA were much lowered. However, the functionalized IEC was less affected by the addition of water and in particular the reaction rate was significantly higher. This suggests that the introduction of ponytails in pDVB_s does not fully protect the catalysts from the action of water, but that limits its effect probably by facilitating the expulsion of its extra amount produced by the reaction.

References

1. Y. Zhang, S. Wei, F. Liu, Y. Du, S. Liu, Y. Ji, T. Yokoi, T. Tatsumi, F.-S. Xiao Nano Today 2009, 4, 135–142.
2. B. M. E. Russbueldt, W. F. Hoelderich Appl. Catal. Gen. 2009, 362, 47–57.
3. Jeřábek, K.; Hanková, L.; Holub, L. J. Mol. Catal. A: Chemical 2010, 333 (1–2), 109–113.
4. L. Hanková, L. Holub, K. Jeřábek J. Polym. Sci. Part B Polym. Phys. 2015, 53, 774–781.
5. Centomo, P.; Bonato, I.; Hanková, L.; Holub, L.; Jeřábek, K.; Zecca, M. Top. Catal. 2013, 56 (9–10), 611–617.

The hydrothermal conversion of cellulose-rich wastes deriving from the papermaking process to levulinic acid as smart opportunity for their re-use and valorization

Domenico Licursi[a],*Claudia Antonetti*[a],*Sara Fulignati*[a], *Alessandro Corsini*[a], *Anna Maria Raspolli Galletti*[a]

[a]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy; domenico.licursi@virgilio.it*

In recent years, the interest of industry has deeply increased towards the exploitation of any kind of waste biomass for the synthesis of new valuable biofuels and bioproducts, in place of the dwindling traditional fossil ones. This approach is strongly encouraged by the Waste Management Policy, which favors thewaste re-use rather than its immediate landfill disposal, by this way achieving significant environmental, social and economic benefits. In this context, the acid-catalysed hydrothermal route for the synthesis of levulinic acid (LA) represents a smart route for the sustainable exploitation of waste biomasses, fully meeting all of the above-mentioned advantages (1). This platformchemical has been classified by the United States Department of Energy as one of the top-12 promising building blocks, being a valuable intermediate for the synthesis of new fuel additives, fragrances, solvents, pharmaceuticals, and plasticizers. The hydrothermal process adopts water as a reaction solvent and very dilute mineral acid (generally H_2SO_4 or HCl) as a homogeneous catalyst for the hydrolysis/dehydration of the cellulose fraction to give LA. Certainly, the fundamental requirement for the choice of the starting feedstock is its high cellulose content, and wastes deriving from the papermaking process fully meet this specification. Most of the national papermaking production of cardboard and tissue paper takes place in the Lucchese territory (~70%). In particular, in the case of the cardboard production, the recycled paper is used as starting feedstock and it needs some preliminary mechanical/chemical treatments for its re-use within the papermaking process. Some of these ones produce considerable rejected waste fractions, such as ‘‘screen rejects”, which include both cellulose fibers and non-fibrous organic contaminants, or ‘‘stickies”, these last representing a shortcoming both for the papermaking process and for the quality of the final product. This waste, which still contains a cellulose fraction, has been hydrolyzed to LA by adopting a one-pot MW treatment, obtaining a LA yield amounting to about 7 wt% (on dry basis), under the best reaction conditions (2). The abundant presence of “sticky” and other impurities represents a strong limit for the optimal exploitation of the cellulose fraction, limiting the acid diffusion towards the cellulose and therefore the use of “cleaner” paper wastes represents a key point for the optimal production of LA, in high yield. Clean virgin cellulose is currently used as starting feedstock for the production of tissue paper, and a significant waste stream (~400-500 tons per year in the Lucchese area)is currently recovered as cellulose powder in the converting section, where the paper coil is unrolled and the sheet is subjected to mechanical operations (stripping, embossing, cutting, etc.) to give the final commercial product (toilet paper and handkerchiefs). The recovered powder is gathered by aspiration and sent to the landfill, because it is too fine to be used again within the same papermaking process. However, it is mainly composed of pure cellulose and, because it has been already mechanically “refined”, it should be more easily hydrolysable to LA, and therefore it represents an ideal feedstock for LA production. The optimization of the hydrolysis reaction of this waste has confirmed the above statements, allowing the LA recovery with very high yields, up to ~ 35 wt% (on dry basis), under the best reaction conditions.

References

1. C. Antonetti, D. Licursi, S. Fulignati, G. Valentini, A. M. Raspolli Galletti, *Catalysts*, Volume 6, pp. 196-225, 2016.
2. D.Licursi, C. Antonetti, M. Martinelli, E. Ribechini, M. Zanaboni, A.M. Raspolli Galletti, *Waste Management*, Volume 49, pp. 469–482, 2016.

Levulinic acid esterification kinetics with ethanol in the presence of Amberlyst-15

V. Russo[a], R. Vitiello[a], R. Turco[a], R. Tesser[a], M. Di Serio[a]

[a]Università degli Studi di Napoli "Federico II", Dipartimento di Scienze Chimiche. Complesso Universitario M.S.Angelo, via Cintia, IT-80126 Napoli.; v.russo@unina.it

The esterification of carboxylic acid with alcohols is a very actual topic of the modern bio-refinery. It is normally performed to produce value-added products, such as solvents and plasticizers (1). This reaction is catalyzed by acid catalysts and occurs with the production of an ester (the main product) and water as by-product. Different catalysts have been already tested in the literature (1,2). Recent findings demonstrate that acid resins, such as Amberlyst-15, show good activity compared to zeolites, for example. This behavior is due to the nature of the catalyst itself. In fact, acid catalysts with high acidity, porosity and surface area are much more active in the reaction itself.
Ethyl levulinate shows promising applications in the field of inks and paints. It is synthetized from levulinic acid and ethanol in the presence of an acid catalyst, normally homogeneous (H_2SO_4).
In the present work, an effort was made to investigate the kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15. Experiments were performed by varying different operative conditions, i.e. stirring rate, temperature, catalyst loading and reactants ratio. As an example, see the effect of temperature in Figure 1.

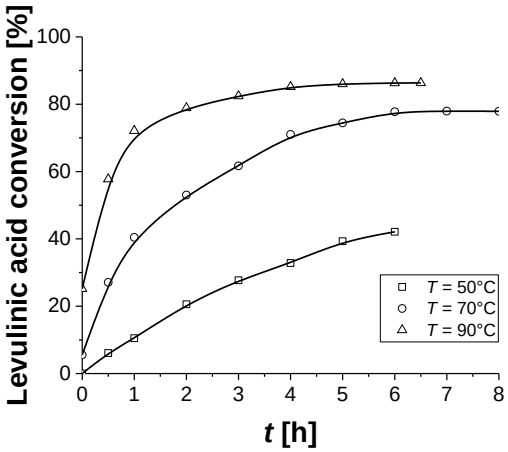


Figure 1. Temperature effect on the levulinic acid conversion. Experiments performed at 600rpm, levulinic acid/ethanol 5:1 mol/mol, 5bar N_2, 2.5wt.% Amberlyst-15.

The collected experimental data were interpreted with reliable models taking into account both the chemical and mass transfer phenomena involved in the reaction network, such as external and internal mass-transfer limitations. The mixed PDE/DAE systems given by the mass balance equations, Eq. 2 (3) were solved with advanced numerical techniques.

$$\frac{\partial C_{i,s}}{\partial t} = \frac{D_{eff,i}}{\varepsilon \cdot x^s} \cdot \frac{\partial}{\partial x}\left(x^s \cdot \frac{\partial C_{i,s}}{\partial x} \right) + \sum_{k=1}^{N} \frac{\rho}{\varepsilon} \cdot r_k \qquad (2)$$

The results can be considered as good starting point for continuous reactors optimization.

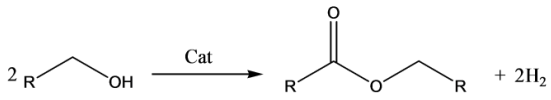
References

1. Fernandes D.R., Rocha A.S., Mai E.F., Mota C.J.A., Teixeira da Silva V. Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts. Applied Catalysis A: General 2012, 425-426, 199-204.
2. Bart H.J., Reidetschlager J., Schatka K., Lehmann A. Kinetics of esterification of levulinic acid with n-butanol by homogenous catalysis. Ind. Eng. Chem. Res. 1994, 33, 21-25.
1. 3. Salmi T., Mikkola J.-P., Wärnå J. Chemical Reaction Engineering and Reactor Technology. New York: CRC Press, 2010.

Dehydrogenative coupling promoted by copper catalysts: a way to upgrade bio-alcohols

Nicola Scotti[a], Federica Zaccheria[a], Claudio Evangelisti[a], Rinaldo Psaro[a], Nicoletta Ravasio[a]
[a] CNR, Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133, Milano; nicola.scotti@istm.cnr.it

Alcohols represent very important molecules for the biomass transformation processes and biorefinery evolution. Taking into account their increasing availability, bio-alcohols are not only products but also represent new feedstock for the chemical industry, e.g. for the production of esters. In this regard, the DHC reaction is an attractive green strategy to directly transform alcohols into symmetrical esters. The process has a very high atom economy and with respect to the traditional esterification methods leads toboth waste reduction and process intensification.This reaction protocol has been mainly studied over expensive noble-metal (e.g. Ru, Os, Re, Pd and Ir) homogeneous complexes(1). Conversely, solid catalysts have been less investigated(2) and Cu heterogeneous systems have already been proposed for the gas-phase conversion of ethanol into ethyl acetate(3) but suffer from low yields (60-65%). Following the successful use of Cu catalysts prepared by Chemisorption-Hydrolysis method in alcohol dehydrogenation reactions(4), we tested a series of systems prepared with the same technique in the liquid phase DHC reaction, in order to develop a simple and robust catalyst able also to expand the substrate scope(5).



Scheme 1. General scheme of DHC reaction

A series of different Cu catalysts have been tested in the liquid phase DHC reaction of 1-butanol into a stainless steel autoclave (Table 1).CuO/ZrO_2 C shows the best performance in terms of activity, allowing one to reach 40% conversion after 3 hours with respect to 16% of CuO/ZrO_2 B and less than 10% of the others.The reaction produces H_2 as co-product thus generating an increase in pressure and freezing the equilibrium position as the substrate is converted (Scheme 1). Therefore by venting the reactor and removing the H_2 produced at regular lapses it is possible to reach 98% yield in 24 h. The activity of this catalyst is remarkable compared with homogeneous and heterogeneous literature on the same topic, considering also that the reaction is highly selective (≥99), carried out on gram-scale (12.6 g of 1-butanol, 170 mmol) and it is solvent- and additive-free. The deep characterization revealed that the high activity of CuO/ZrO_2 C is has to be ascribed to the intimate contact between copper phase and zirconia that form acid-base pairsbased on CuO Lewis acid sites and ZrO_2 strong basic sites. CuO will promote dehydrogenation of butanol and activate the aldehyde towards the attack of an alcohol molecule activated by the basic sites of ZrO_2.CuO/ZrO_2 C revealed to be also extremely robust and versatile. It is reusable up to four times without observing any Cu leaching and significant loss in activity. Moreover high conversions (93%) and selectivities (98-99%) in 24 h were obtained for C3-C8alcohols. Remarkable is also the yield of ethyl acetate (87%) obtained from ethanol, in particular if compared with the others catalytic systems reported in the literature.

Catalyst (400 mg)	SSA (m^2/g)	C (%)	S (%)	Y (%)
CuO/SiO_2	318	4	90	3
CuO/Al_2O_3	126	10	>99	10
CuO/ZrO_2 A	3	9	>99	9
CuO/ZrO_2 B	88	16	>99	16
CuO/ZrO_2 C	314	40	>99	40
CuO/ZrO_2 C*	314	98	>99	98

250 °C; N_2=1 bar; 1-butanol=170 mmol; t=3h; *t=24h

Table 1. DHC of 1-butanol to butyl butyrate

References

1. S. Gowrisankar, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.*, **2011**, 50, 5139.
2. S.K. Moromi, S.M. A. Hakim Siddiki, M.A. Ali, K. Kon, K. Shimizu, *Catal. Sci. Technol.*, **2014**, 4, 3631.
3. P.C. Zonetti, J. Celnik, S. Letichevsky, A.B. Gaspar, L.G. Appel, *J. Mol. Catal. A Chem.*, **2011**, 334, 29.
4. F. Zaccheria, N. Ravasio, R. Psaro, A. Fusi, *Chem. Eur. J.*, **2006**, 12, 6426.
5. N. Scotti, F. Zaccheria, C. Evangelisti, R. Psaro, N. Ravasio, *Catal. Sci. Technol.*, **2017**, 7, 1386.

Succinic acid production from arundo donax hydrolysate for bio-based poly(butylene succinate) synthesis

Rosa Turco[a], Martino Di Serio[a], Marcella Mazzocca[a], Vincenzo Russo[a], Riccardo Tesser[a], Rosa Vitiello[a], Donatella Cimini[b], Chiara Schiraldi[b]

[a]University of Naples Federico II, Department of Chemical Sciences, Complesso Universitario di Monte Sant'Angelo, 80126 Naples, Italy;
[b]University of Campania Luigi Vanvitelli, Department of Experimental Medicine, Via Santa Maria di Costantinopoli 16, 80138 Naples, Italy; rosa.turco@unina.it

The US Department of Energy (DOE) included succinic acid (SA) in the "Top 10" list of biomass-derived compounds, considering its high potential as building block in the field of the industrial chemistry (1). In fact, this dicarboxylic acid with four carbon atoms (1,4-butanedioic acid) represents an important precursor molecule for many chemical derivatives, used for food and pharmaceutical products, solvents, biodegradable polymers, surfactants and detergents (2). Nowadays SA is mainly produced by crude oil, starting from n-butane/butadiene via maleic anhydride. Due to its independence of petroleum, environmental benefit and reduction in CO_2 emissions, biotechnological production of SA from renewable feedstocks is gaining increasing attention in the last years. SA is an intermediate of the tricarboxylic acid cycle and one of the end products of the anaerobic metabolism. Extensive efforts have been made to optimize the SA biotechnological production, and they have principally concerned the development of biocatalysts to improve the productivity and the optimization of the downstream process to separate SA from the fermentation broths to minimize the process costs (3). The downstream purification costs affect about 60% of the total production costs. Furthermore, very high purity is often required in these cases. To this end, several methods of purification and separation, including electrodialysis, precipitation and extraction, have been studied and developed. Many companies such as Myriant, Everdia, BioAmber and Succinity established bio-based production platforms for the conversion of purified sugars to SA.
This work aims to provide an integrated process based on the biotechnological production of SA using a lignocellulose biomass (Arundo Donax) as raw material, for the synthesis of a biodegradable plastic, i.e. poly(butylene succinate) (PBS). The novelty lies in the type of raw material used, a harvested waste, to produce added value chemicals such as PBS. SA separation and purification procedure was developed and integrated to the fermentation process by a vacuum distillation at pH=4 to remove the volatile byproducts after a treatment with activated charcoal, followed by a final crystallization from mother solution. PBS was synthesized using SA, recovered and purified directly from its fermentation broth through the downstream protocol developed and optimized in this study. The synthesized polymers showed physical and mechanical properties comparable with a commercial PBS derived by crude oil, so highlighting the suitability of the proposed process.

References

1. J.M. Pinazo, M. E. Domine, V. Parvulescu, F. Petru, Catal. Today, 239 (2015) 17-24.
2. C. Wang, W. Ming, D. Yan, C. Zhang, M. Yang, Y. Liu, Y. Zhang, B. Guo, J. Xing, Bioresource Technol., 156 (2014) 6-13.
3. D. Cimini, O. Argenzio, S. D'Ambrosio, L. Lama, I. Finore, R. Finamore, O. Pepe, V. Faraco, C. Schiraldi, Bioresource Technol., 222 (2016) 355-360.

The history of the journal "La Chimica e l'Industria"

Ferruccio Trifirò

Professor emeritus University of Bologna;e-mail: ferruccio.trifiro@unibo.it

The magazine "La Chimica e l'Industria", current official journal of the Italian Chemical Society (SCI), was created in 1919 with the name "Giornale di Chimica Industriale" with the aim of helping to let born also in Italy a significant chemical industry, as it had been in Germany over the decades before the First World War, trying to intensify the relationship between academia and industry. The journal wsas founded by the Society of Industrial Chemistry of Milano.
From March 1920 to December 1934, the magazine changed its name to "Giornale di Chimica Industriale e Applicata" and from 1935 until now the magazine changed its name in "La Chimica e l'Industria" The largest expansion of the magazine was in the years around 1963; this because in addition to the fact that Natta received that year the Nobel Prize for Chemistry, it was witnessed at that time to a large development of the Italian chemical industry. Since its birth until 1970, the magazine was the journal on which largely the industrial chemists of academia and of industry published essentially original articles and also reported informations on the Italian chemical industry. Natta from 1923 to 1954 on 207 published papers, wrote in La Chimica e l'Industria 42 original papers. It can certainly be said that if you want to have information about the Italian chemical industry and the innovations in the industrial chemistry of those times, you can read the magazine. For example, in Trincheri's book on the history of Italian chemical industry, there are many quotes of articles published in the magazine. After 1971, the magazine was opened not only to original scientific articles of industrial chemistry, but also to scientific reviews on other fields of chemistry. In 1994, with prof Ivano Bertini as director (president SCI), it was officially declared that the magazine did not more publish original scientific articles, but it had to be a review of all chemistry. With Trifirò, director from 1996 till now, the strategies of the previous directors have been confirmed, but the importance of having articles from the industrial world to foster innovation has also been emphasized. In 2000, a major revolution took place with the publication of the magazine on the site web. In 2014, there was a further change with the unification with the Order of Chemists and the publication of the two magazines together and then in 2015 with the publication of a single magazine. In 2017 the magazine returned to the Chemical Society and it is published only on the web. From 1967 to 1980 Trifirò on the journal published only 15 original works on a total of 91 published works, most in English, and he was one of the first to do it. From 1981 to 1990 he did not send more original articles, but only 6 scientific reviews of his work. From 1991 to 1995 began publishing 7 reviews of some sectors of Italian chemical industrie. Since 1996 when he became director of the journal till now he wrote 290 articles (as editorials and reviews of technologies of the chemical industry).

Comunicazioni Flash

Polymer Electrolytes Prepared by Industrially Compatible Processes for Renewable Energy Storage in Sodium Batteries

Francesca Coló[a], *Federico Bella*[a], *Jijeesh R. Nair*[b], *Claudio Gerbaldi*[a]

[a]*GAME Lab, CHENERGY Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Torino, Italy;*
[b]*Helmholtz-Institute Münster (HI MS) IEK-12: Ionics in Energy Storage,Corrensstraße 46, 48149 Münster, Germany;*
e-mail: francesca.colo@polito.it

With the fast development of renewable energy sources, such as wind and solar plant, large-scale and high energy storage system are becoming extremely important to realize the load leveling of these intermittent energies into the grid. The most promising technology for that are secondary batteries (rechargeable) because high energy conversion, simple design, flexibility, easy to maintain. In order to meet the low cost policy in the market, sodium based secondary batteries are the best deal actually. However, the currently technology of batteries use liquid electrolytes as ion transport media, and these liquid electrolytes are based on organic solvents that are toxic and volatile, and the use of these flammable liquids in batteries raises safety concerns. The most powerful solution on it is switch on all solid state material such as polymer films, ceramics, etc…
Here, we offer an overview of our recent developments on polymer electrolytes for Sodium-ion batteries. Polymer electrolytes were prepared through different techniques, exploiting techniques very easily to applied on an industrial point of view, simple casting (1) and UV-curing (2). All samples were thoroughly characterized in the physico-chemical and electrochemical viewpoint. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation at ambient conditions. Electrochemical performances in lab-scale devices are presented, evaluated by means of cycling voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials (prepared by water-based procedures with green carboxymethylcellulose as binder).
Work on Na-ion polymer batteries for moderate temperature application is at an early stage, only lab-scale cells were demonstrated so far. Nevertheless, with the appropriate choice and optimisation of electrode/electrolyte materials (and succesfull combination thereof), the intriguing characteristics of the newly developed SPEs here presented postulates the possibility of their effective implementation in safe, durable and high energy density secondary Na-based polymer devices conceived for green-grid storage and operating at ambient and/or sub-ambient temperatures.

References

1. F. Colò, F. Bella, Jijeesh R. Nair, M. Destro, C. Gerbaldi, *Electrochim. Acta* 174 (2015) 185-190.
2. F. Bella, F. Colò, Jijeesh R. Nair, C. Gerbaldi *ChemSusChem*, 8 (2015) 3668-3676.

Thin film of Black-Gold by electrodeposition, for jewellery making

Antonio De Luca[a], *Emanuele Piciollo*[b], *Claudio. Picchi*[b],*Alessio Ceccarini*[c], *Emanuele Salvietti*[a d], *Francesco Di Benedetto*[e], *Stefano Caporali*[d f],*Stefano Martinuzzi*[d] *and Massimo Innocenti*[a d]

[a] *Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto Fiorentino, Italy;*
[b]*LEM s.r.l. Socio Unico, Leo Valiani, 55/59 Levane 52021 Bucine (AR), Italy;*
[c] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via G. Moruzzi 3, 56124 Pisa, Italy;*
[d]*INSTM, via G. Giusti 9 ,50121, Firenze(FI), Italy;*
[e]*Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4,50121, Firenze (Italy);*
[f] *Dipartimento di ingegneria industriale, Università di Firenze, via S. Marta3, 50139 Firenze ((Italy);*
e-mail: antonio.deluca@unifi.it

In the making of jewellery the most common types of gold colours used are white gold and yellow gold. Anyway lots of other colours of gold are also possible to achieve by electroplating.
Nowadays purple gold, black gold and blue gold are the gold colors more interesting and researched by fashion market.
There are two electrochemical deposition processes used to obtain such colours: the first one is by forming a surface coating on gold, also referred to as Patination of Gold. The second process consists of the formation of gold metal alloys also referred to as Intermetallic Compounds.
The black gold thin films can be prepared by more methods, utilization of amorphous carbon during Plasma Assisted Chemical Vapour Deposition process, controlled oxidation of carat gold containing chromium or cobalt and electrodeposition processes.
We investigate mainly thin films obtained by electrodeposition processes.
Electrodeposition using black Rhodium or Ruthenium added to gold electroplating solution is one way. Electroplating solutions containing Ruthenium give a slightly harder black coating as compared to electroplating solutions containing Rhodium. We present some electrochemical results about the formation of thin films of black gold and their morphological characterizations by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).
We're going also to evaluate a correlation between films electrodeposited from different plating baths and corrosion resistance of the films themselves.

Study of Fenton reactor in a wastewater treatment plant

Grazia Leonzio

Department of Industrial and Information Engineering and Economics, University of L'Aquila, Via Giovanni Gronchi 18, 67100 L'Aquila, Italy

Fenton technology is a promising and alternative method for wastewater treatment an environmental friendly method for pollutants treatment (1). In scientific literature, there are several applications of Fenton reactor for wastewater treatment, such as textile wastewater, laboratory wastewater, industrial effluents, cosmetic wastewater, dye wastewater, pesticides, fermentation brine from green olives, pharmaceutical wastewater, cork cooking wastewater, pulp mill effluents, and phenol degradation (2). In all cases, researcher's pin-point for a percentage of residual hydrogen peroxide remaining unreacted at the outlet of the oxidation reactor or at the exit of the treatment plant is analyzed. In this research, a study of Fenton reactor in a wastewater treatment plant is carried out. The plant processes hazardous liquid waste and not, and different treatments are present: biological, physical/chemical, distillation/evaporation. The most important treatment is the Fenton reactor used to reduce the odorigeno impact and to improve the operation of biological section. H_2SO_4 is added until a value of pH equal to 4 and then $Ca(OH)_2$ is added until a value of pH equal to 10.5. In the distillation/evaporation treatment, wastes with high concentrations of volatile solvents, salts, metals and organic substances not disposed in the biological section are treated. However, the feed of column distillation is excessively diluted, so another configuration of the plant is developed: all evaporated of concentrator, dryer and multiple effect (collected in D41 vessel) are sent to the Fenton reactor and not to the distillation. The response of Fenton reactor to this change is analyzed in this study, infect in the normal operation only the residue of column distillation is sent to the Fenton for the subsequent biological treatment. An ANOVA analysis is carried out to this purpose, using the Yates' algorithms for the estimation of main factors. Concentration of H_2O_2, concentration of FeSO4, evaporated of D41 vessel are considered as factors. The chosen responses are: values of chemical oxygen demand (COD) and oxygen uptake rate in the outlet of the Fenton. A 2^3 full factorial design with 8 tests is developed. The statistical significance is checked by the F-value and p-value at the 5% of significance level. In laboratory experiments, total COD concentration is analyzed using the Hach Lange test kit LCK (according to the standard method ISO 6060-1989). OURs measurements are carried out with a digital respirometer. Anova analysis is carried out in two different days and the effect of different days is confused with the effect of third order interaction. Four factorial experiments are carried out in order to evaluate the presence of similar results. Results show that for the values of COD the concentration of H_2O_2 has a negative effect, the vessel D41 does not modify the yield of the reactor and only in one case is reduced. The interactions of higher order produce a negative effect; different feeds are also significative. For the biodegradability of the sludge, the concentration of $FeSO_4$ has a positive effect only in one case. The evaporated of D41 vessel has manly a positive effect: the evaporated of the plant increase the biodegradability and different feeds have mainly a positive effect.

References

1. Huang et al., 2017. Combination of Fenton processes and bio-treatment for wastewater treatment and soil remediation, Science of the Total Environment, 574, 1599–1610.
2. Hodaifa et al., 2013. Optimization of continuous reactor at pilot scale for olive-oil mill wastewater treatment by Fenton-like process, Chemical Engineering Journal, 220,117–124.

Isoprene production from methanol: an investigation on the reaction mechanism.

Giada Innocenti[a,b], Andrea Malmusi[a,b], Matteo DellaPasqua[a,b], J. Velasquez Ochoa[a], Fabrizio Cavani[a,b]

[a]Dipartimento di Chimica Industriale "Toso-Montanari", Università di Bologna, Bologna, Italia;
[b]Consorzio INSTM, UdR di Bologna, Firenze, Italy;
e-mail: giada.innocenti2@unibo.it

2-Methyl-1,3-butadiene, usuallycalled isoprene (IPE), is among the most important building blocks for the production of synthetic rubber. (1) One of the processes used for IPE production relies on the Prins reaction between isobutene and formaldehyde over acid catalysts (2,3). The main drawback of this process is the use of formaldehyde, which is carcinogenic and can be precursor of heavy compounds finally leading to catalyst deactivation.
In this work, IPE production through methanol-isobutene coupling is presented, opening the way for an alternative route to the nowadays-used industrial two-pot reaction. (4, 5)
The final aim of this study is to dig up into thecoupling reactionmechanism between methanol and isobutene over Al/P/O-based catalyst.
Amorphous Al/P/O catalystwas synthesized by a co-precipitation method followed by drying and calcination. (2) The catalysts were tested at 400 °C in gas-phase, using a continuous-flow glass reactor, feeding methanol and isobutene in ratio 1/6, at different contact times. Supplementary experiments, aimed at investigating the behaviour of the reaction products, were carried out feeding either dimethyl ether (DME) and isobutene or IPE only. Thanks to a comparative analysis of all the results, it was possible to hypothesize the reaction scheme reported in Figure 1. The reactivity tests have pointed out that IPE is produced along with 2-methylbutenes by methanol, as well as DME, and isobutene direct condensation. IPE might also undergo a consecutive decomposition to either retro-Prins products or 2-methylbutenes.

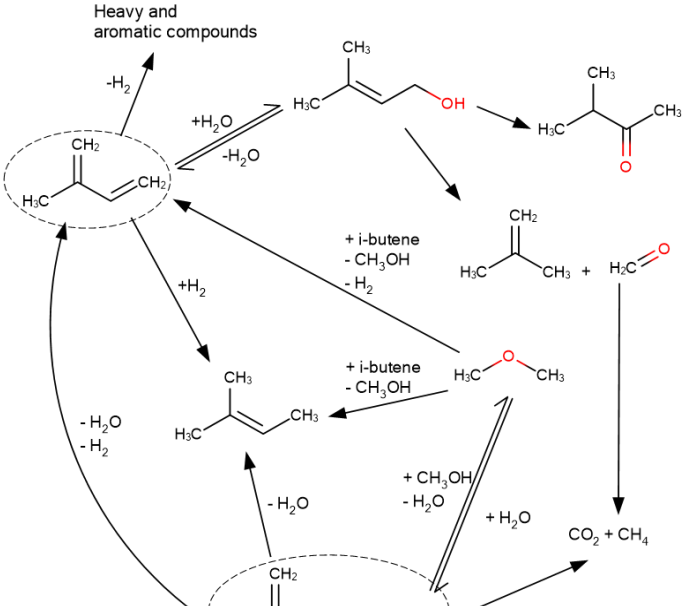


Figure 3. Simplified reaction scheme of isobutene-methanol coupling to isoprene.

Aknowledgements: Versalis SpA is gratefully acknowledged for sponsoring part of the research described

References

1. H. M. Lybarger, Isoprene in Kirk-Othmer Encyclopedis of Chemical Technology, John Wiley & Sons, Inc., 2000.
2. V. L. Sushckevic et al. Applied Catalysis A: General, 441-442, (2012), 21-29.
3. V. L. Sushckevic et al. Catal. Sci. Technol., 2016, 6, 6354.
4. P. Y. Gokhberg et al., USP 4147736, (1977).
5. G. O. Ezinkwo, et al Catal. Suistainable Energy, 2013, 1, 100-111.

.

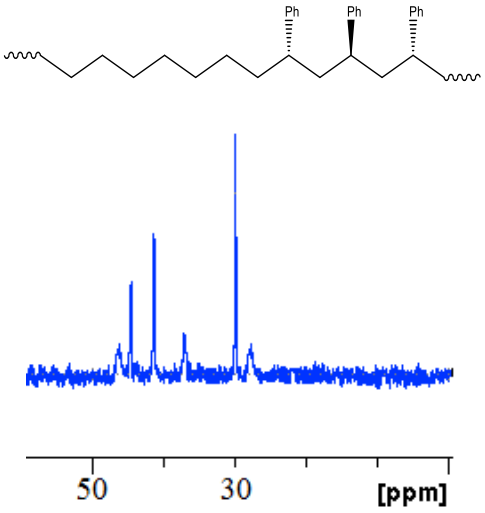
Diblock copolymer ethylene-syndiotactic styrene

David Hermann Lamparelli[a], Antonio Buonerba[a], Nunzia Galdi[a], and Leone Oliva[a]

[a]Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università di Salerno, via Giovanni Paolo II, 132 - 84084 Fisciano (SA) Italia; dlamparelli@unisa.it

The one-pot synthesis of ethylene-styrene (ES) copolymers, where an isotactic polystyrene sequence is jointed to an alternating ES sequence, has been recently obtained by the quasi-living polymerization at low temperature using the catalyst zirconocene rac-methylenebis(1-indenyl)zirconium dichloride activated by methylaluminoxane (MAO) (1).

Keeping in the mind the idea of makingnew ES architectures copolymer, we have carried out the synthesis, through the living polymerization at low temperature, of a ethylene-styrene diblock copolymer with unprecedented structure, containing stereoregular polystyrene blocks.



Aliphatic regione of the ^{13}C- NMR of the toluene soluble fraction

The key of the achievement is the homogenous polyinsertion catalysis by $CpTiCl_3$ at 0 °C combined with MAO and a judicious choice of monomers feed composition.

^{13}C nuclear magnetic resonance analysis of the boiling toluene soluble fraction (fig.) indicates the contemporary presence of syndiotacticstyrene sequence (**sPS**) and polyethylene sequence.

The length of the ethylene sequence, estimated by the NMR resonances, increases with the growth of the ethylene concentration in the monomer feed composition.

The atomic force microscopy (**AFM**) techniques shows how these materials in the solid state organize themselves into nanostructures depending on the comonomers composition.

References

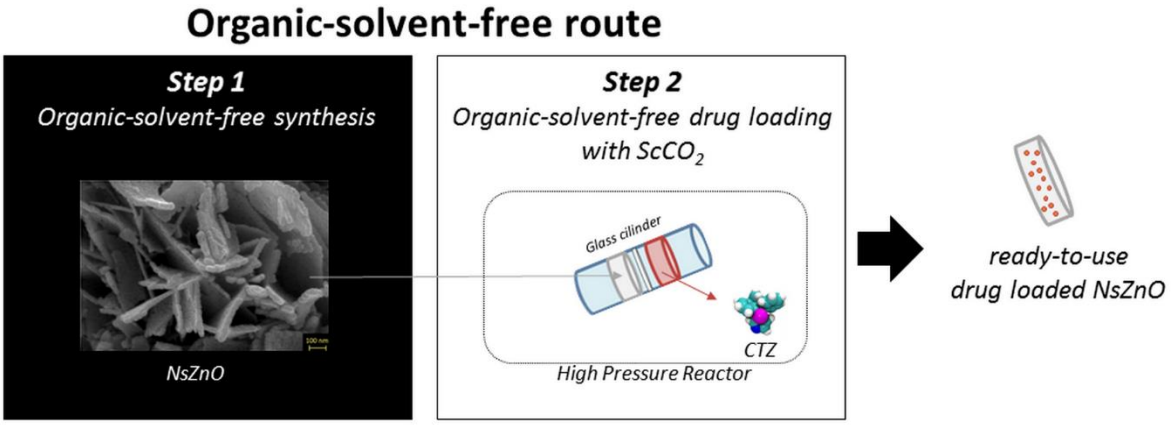
1. N. Galdi, A. Buonerba, P. Oliva and L. Oliva, *Polym. Chem*., 2014, 5, 3045-305.

An organic-solvent-free route to obtain nanostructured zinc oxide-based reservoir of clotrimazole.

Federica Leone[a], *Andrea Gignone*[a], *Silvia Ronchetti*[a], *Roberta Cavalli*[b], *Luigi Manna*[a], *Mauro Banchero*[a] *and Barbara Onida*[a]

[a]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Torino, Italy;*
[b] *Department of Drug Science and Technology, Universitá degli Studi di Torino, Via Pietro Giuria, 9, 10125, Torino, Italy; federica.leone@polito.it*

An organic-solvent-free route to obtain nanostructured zinc oxide (NsZnO) reservoir of clotrimazole was studied. Two different NsZnO materials were synthesized, selecting wet chemical approaches without any organic solvents: chemical bath deposition and a soft-template sol-gel method.
For the first time, loading of clotrimazole (CTZ) in a ZnO carrier by impregnation using supercritical CO_2 as solvent was studied. The NsZnO materials were characterized, before and after drug loading, by FESEM, XRD, nitrogen adsorption isotherms, TGA, DSC, in order to elucidate their morphological and physico-chemical properties.
CTZ was dispersed in the NsZnO carrier in amorphous form, with a maximum loading of 17 % w/w. *In vitro* drug-release was investigated, revealing that the NsZnO carriers can deliver clotrimazole, ensuring a fast release of a larger drug amount when compared to the solid crystalline drug. This might play a key role in several biological applications where the bioavailability of poorly-water-soluble drugs is still a challenging issue.



Cool Roofing, where chemistry indirectly helps environment

Marino Malavolti[a], *Antonietta Schirò*[b], *Marco Cerra*[c]

[a]*Synthesis Dept. Vinavil SpA;*
[b]*Head Coating Dept. Vinavil SpA;*
[c]*R&D Director Vinavil SpA; m.malavolti@vinavil.it*

In the inhabited part of planet where the ambient temperatures are high, a lot of energy is spent for air conditioning the houses, the figures are striking, thus a way to reduce this energy was found.
As in these areas the roofs are not made by tiles but they are flat or in general with a cement finish like the external walls, the idea was to cover the upper part of the houses with a white highly reflecting paint in order to reduce the absorption of the sun rays
The elastomeric roof covering has very similar characteristics to a mural painting. They are applied by spraying or roller on newly installed roofs or on existing surfaces.
The properties and performance of the elastomeric roof covering have a very similar appearance and viscosity to mural paintings, but a major difference is that the elastomeric "Roof Coating" coatings are, as the name suggests, more elastic and give the ability to expand and contract. This versatility can make the film very tough during temperature changes because it expands with heat and contracts to cool, reducing the likelihood of breaking.
Another big difference is the application thickness, mural paintings usually have a dry film thickness around 70-100 microns, while the elastomeric roofing applications have a dry film thickness of about 450-500 microns.
For this kind of very demanding application a special type of polymers have been designed: the most important requirements is to have a high durability on the outside for long exposure periods,. in addition due to temperature variations and natural elements such as snow and rain, the roofs are subject to humidity fluctuations, seismic expansion, wind and building vibration lifting then a very high flexibility is required.
Another feature requested is to withstand with occasional pedestrian traffic so the polymer for elastomeric roofing coatings must be flexible but at the same time resistant to static and dynamic pressures
Another important requirement is the reflectivity of infrared and ultraviolet rays. These coatings are mainly pigmented in white or light colors to maximize the amount of solar radiation to reflect. A high-performance coating can reflect 80% of solar radiation. The reflection of the liner helps keep the building cooler and reduce energy costs. To maintain this requirement, they must also have excellent resistance to dirt, to keep the coating always white and reflectant.
In this presentation we will describe the characteristics of elastomeric coatings for roofs formulated with acrylic or styrene acrylic emulsion polymers, which have many advantages and high performance. Emulsion polymers are able to provide better adhesion to a variety of substrates, low temperature low water absorption and very low dirt pick-up.

Integrated catalytic process for biomass hydrolysis: a comparison of different pretreatments and catalysts

Mattia Melloni[a], Fabrizio Cavani[a], Anna Maria Raspolli Galletti[b], Hilda Gomez Bernal[b], Claudia Antonetti[b]

[a]Department of Industrial Chemistry, University of Bologna, Bologna, 40136, Viale del Risorgimento 4, Italy;
[b]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, 56124, Via Moruzzi 13, Italy;
mattia.melloni2@unibo.it

The conversion of lignocellulose biomass into valuable chemicals is one of the pillars of the biorefinery, the aim of which is to develop integrated processes for the transformation of renewables collected from agricultural, forestry and urban waste into "bio-platform molecules". For these reasons, there is a great interest in developing reusable solid acid catalysts, which are effective in cellulose transformation, in place of the traditional processes that make use of mineral acids.
The starting point of the transformation chain is the deconstruction of the lignocellulose and depolymerization of the hemicellulose and cellulose to give monosaccharides, or even transform sugars into other valuable bio-based building blocks. Difficulties derive from both the resistant lignin sheath and the tight packing of cellulose chains. This implies the need for pretreatments procedures, aimed at improving the accessibility of catalytic acid sites.
The aim of this work is to compare the performance of metal phosphates catalysts in cellulose and lignocellulose (conifer wood sawdust) hydrolysis, after pretreatment of the biomass with different procedures.The catalysts tested in hydrolysis reaction were based on Zr/P/O and Nb/P/O systems, previously tested in other hydrolysis reaction(1) and showing interesting and diversified performances, thanks to their peculiar acidic properties. We compared two different types of pretreatment: a mechanical pretreatment, in which the substrate was subjected to a 48-hours treatment in a high-energy ball mill, and a thermal pretreatment, in which biomass was autohydrolyzed at 180°C for 1 hour in a monomodal microwave reactor. Results of tests conducted with metal phosphate catalysts on cellulose and lignocellulose, either as such or after the two different treatments, showed that pretreatments were effective in facilitating the hydrolysis: in particular, with pretreated substrates, we observed an important improvement of catalytic performance. However, autohydrolysis in microwave reactor permitted to obtain better conversion and yields to monosaccharides and successive decomposition products, compared to the ball-milled substrate.
As regards catalytic behaviors, the differences of performances between the two metal phosphates can be explained by invoking both the different total concentration and type of acid sites: we evaluated the total concentration of acid sites by means of ammonia TPD and the type of acidity (Brønsted/Lewis acid site ratio) by means of FT-IR adsorption of pyridine.It is possible to conclude that: the Zr/P/O system has a higher concentration of total acid sites, that results into a higher conversion of the biomass, in particular of the cellulosic fraction; instead, the Nb/P/O system presents a higher Brønsted/Lewis acid sites ratio, that reduces the production of monosaccharides in favor of successive decomposition products.

References

1. C. Antonetti, M. Melloni, D. Licursi, S. Fulignati, E. Ribecchini, S. Rivas, J. C. Parajo, F. Cavani, A. M. Raspolli Galletti, App. Catal B: Environ., 2017, **206**, 364-377.

Removal of non-degradable organic compounds from water with photocatalytic nanocomposite aerogels

Wanda Navarra[a], *Olga Sacco*[a], *Vincenzo Vaiano*[c], *Diana Sannino*[c],*Christophe Daniel*[a,b], *Vincenzo Venditto*[a,b]

[a]*University of Salerno, Department of Chemistry and Biology, A. Zambelli, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy;*
[b]*INSTM Research Unit, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA) Italy;*
[c]*University of Salerno, Department of Industrial Engineering, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy;*
e-mail: wandanavarra@gmail.com

To remove the non-degradable organic compounds from wastewater several methods like adsorption, filtration and chemical oxidation, are used. These common treatment processes have the disadvantage of not degrading but only capturing contaminants, often creating secondary pollution. A possible alternative is to use heterogeneous photocatalysis which are able to degrade these soluble organic contaminants. The photocatalyst, in form of nanopowder or nanocomposite, is generally dispersed in a slurry reactor as suspended powder. This process has the following drawbacks, the separation of nanopowders from purified water is very expensive and the use of powder photocatalysts in slurry reactors damages reactor recirculation pumps. A possible solution to overcome this technical limitation is to fix the photocatalyst nanopowder on bulky organic or inorganic support materials.
Highly attractive support materials for photocatalysts are high porosity monolithic aerogels which can be easily obtained by drying of physical gels with supercritical CO2. The preparation of physically cross-linked aerogels has been reported for different thermoplastic polymers such as polyethylene, syndiotactic polystyrene (s-PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(ether-ether-ketone) or poly(lactic acid). A particular class of monolithic physically cross-linked aerogels, having the peculiarity that the crystallites forming the aerogel physical knots are nanoporous crystal phase, can be achieved by using PPO and s-PS. The PPO and s-PS crystalline nanoporous aerogels are able to rapidly absorb volatile organic compounds (VOCs), mainly halogenated or aromatic hydrocarbons, from water and air, also when present at very low concentrations (2).
This contribution will focus on the preparation and characterization of composite monolithic aerogels based on s-PS and N-doped TiO2 (NdT) photocatalyst. In detail the photocatalyst activity of well dispersed NdT nanoparticles in s-PS crystalline nanoporous (NdT/s-PS) aerogels will be compared with that of the pure NdT powder. The higher photocatalyst activity of NdT/s-PS aerogles will presented and discussed (3).

References

1. Daniel C, Longo S, Ricciardi R, Reverchon E and Guerra G, Monolithic nanoporous crystalline aerogels. Macromol Rapid Commun 34:1194–1207 (2013).
2. Daniel C, Sannino D and Guerra G, Syndiotactic polystyrene aerogels: adsorption in amorphous pores and absorption in crystalline nanocavities. Chem Mater 20:577–582 (2008).
3. Vaiano, V., Sacco, O., Sannino, D., Ciambelli, P., Longo, S., Venditto, V., and Guerra, G. (2014). "N-doped TiO2/s-PS aerogels for photocatalytic degradation of organic dyes in wastewater under visible light irradiation." Journal of Chemical Technology and Biotechnology, 89(8), 1175-1181.

Heterogeneous photocatalytic processes for the abatement of N-containing pollutants from waste water

Veronica Praglia[a], *Elnaz Bahadori*[a], *Matteo Compagnoni*[a], *Gianguido Ramis*[b], *Ilenia Rossetti*[a]

[a]*Dip. Chimica, Università degli Studi di Milano and INSTM Unit Milano-Università, Milan, Italy;*
[b]*Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, Genoa, Italy;*
veronica.praglia@studenti.unimi.it; ilenia.rossetti@unimi.it

Since the last four decades, the viability of photocatalytic degradation of organic compounds in water streams has been demonstrated. Nitrogen containing compounds, such as dyes, pesticides, drugs, etc. as well as inorganic ammonia (1), nitrites and nitrates (2), are harmful contaminants for drinking water and ground water (3). These compounds are particularly relevant in agriculturally intensive zones and in the case of some industrial processes involving e.g. nitration reactions. Therefore, the development of effective methods for the abatement of these harmful pollutants from waste waters and from hydric resources is a challenging task. Different configurations for solar TiO_2 photocatalytic reactors have been used (4), however pilot and demonstration plants are still countable.
This work represents the photocatalytic processes for the abatement of N-containing compounds focusing mainly on the photoreduction of nitrate ions and the photooxidation of ammonia in semibatch mode, aiming at maximum selectivity towards N_2(5). Innovative photoreactors were specifically designed and optimized for this application.
Different photocatalysts have been prepared with two different methods and their photocatalytic performance has been compared with commercial nanostructured TiO_2 (P25). TiO_2 has been prepared in nanosized form by using an innovative flame pyrolysis (FP) approach, and mesoporous $TiO_2$was prepared by sol-gel method. Pd has been in case added TiO_2 by post synthesis impregnation. The physical/chemical properties of the photocatalysts were studied by means of XRD, BET and UV-Vis spectroscopy.
The results of both photooxidaton and photoreduction of photocatalysts imply that the flame pyrolysis procedure is a viable technique for the preparation of nanosized $TiO_2$for this application, leading to ca. double conversion with respect to commercial samples. Furthermore, the addition of a small amount of Pd (0.1 wt%), likely enhanced the lifetime of the photoproduced charges by electron trapping and resulted in higher conversion in almost all photocatalysts. However, the best performance was obtained by Pd doped on TiO_2 (FP) especially in the photooxidation process with conversion up to 31% after 5h and selectivity up to 100%.
The specific configuration of designed photoreactor, enhanced the uniform mixture of catalyst and light distribution and opens possibility for further optimization for scale up in order to be used with direct sunlight.

Keywords:
Photoreduction, Photooxidation,N-containing compounds, Waste water treatment, TiO_2, Flame pyrolysis

Acknowledgements: Fondazione Cariplo (grant 2015-0186"DEN - Innovative technologies for the abatement of N-containing pollutants in water") is gratefully acknowledged.

References

1. Lee J., Park H., Choi W., 2002, Environ. Sci. Technol., 36, 5462.
2. Nolan B.T., Puckett L.J., Ma L.W., Green C.T., Bayless E., Malone R.W., 2010, J. Environ. Qual., 39, 1051.
3. Burow K.R., Nolan B.T., Rupert M.G., Dubrovsky N.M., 2010, Environ. Sci. Technol., 44, 4988.
4. Bukowski J., Somers G., Bryanton J., 2001, *J. Occup. Environ. Med.*, 43, 377.
5. Compagnoni M., Ramis G., Freyria F.S., Armandi M., Bonelli B., Rossetti I, 2017, J. Nanosci. Nanotech, 17, 3632.

The upgrading of bio-alcohols: Production of added-value chemicals by the gas-phase (oxi)dehydration of 1-butanol over V/P/O catalysts

Francesco Puzzo[a], *Giulia Pavarelli*[a], *Carlo Lucarelli*[b], *Fabrizio Cavani*[a]

[a] *ALMA MATER STUDIORUM – University of Bologna, department of Industrial chemistry "Toso Montanari", Viale del Risorgimento 4, 40136 Bologna;*
[b]*Dipartimento di Scienza e Alta Tecnologia, Università degli studi dell'Insubria, 22100, Como, Italy*

During latest years bio-alcohols, such as 1-butanol, are being studied as platform molecules alternative to the fossil-based building blocks. This alcohol can be used as the reactant for the production of butenes(1) and maleic anhydride (MA)(2), as illustrated in figure 1. In this work, we report about the catalytic performance of vanadyl phosphate, α_1-$VOPO_4$ (VPD),for the synthesis of butenes and MA from 1-butanol. The presence of acid and redox sites on the surface of VPD [3] allowedus to use it as a multifunctional catalyst for the dehydration and oxidation steps.By varying catalyst textural properties and reaction conditions, it was possible to modify the catalytic behavior, thus the selectivity into olefinsand MA. The catalytic performances were tested by feeding 1 mol% of 1-butanol either in helium or in air, at different temperatures. Under anaerobic conditions the formation of 1- and 2-butenes and a non-negligible amount of butyraldehydewas observed. However, C balance was poor, because of the formation of heavy compounds on catalyst surface, which also were responsible for VPD deactivation at high temperature. The performance of VPD catalyst in the presence of air, summarized in figure 2; at low temperature, the catalytic behavior was similar to that one observed in absence of air. However, in this case, complete conversion was achieved already at 260°C, with 97% selectivity to butenes, no lack in C balance and no deactivation. At temperatures higher than 330°C, wenoticed the formation of CO, CO_2, maleic anhydride (MA), other oxygenated compounds such as acrylic and acetic acid, furan and phthalic anhydride. At 440 °C, the highest selectivity into MA (36%) and CO_x (38%) were achieved. The characterization of the spent catalysts by Raman spectroscopy showed the presence of carbonaceous compounds, especially in the case of tests carried out without oxygenin feed, and both α_1 $VOPO_4$ and $(VO)_2P_2O_7$ (VPP) compounds. The formation of the VPP during reaction in air can be attributed to the strong interaction of 1-butanol with the catalyst surface and the development of a redox equilibrium between the gas-phase and the V ions involved in the reaction. In conclusion, by varying temperature and reaction environment, it is possible to modify the catalytic behavior of α_1-$VOPO_4$in order to address the transformation of the alcohol into olefins and/orMA. Oxygen plays a fundamental role for the entire process, because it disfavors the formation of heavy compounds on the catalytic surface and also supports the oxidation reactions.

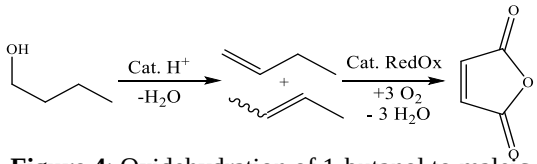


Figure 4: Oxidehydration of 1-butanol to maleic anhydride via butenes.

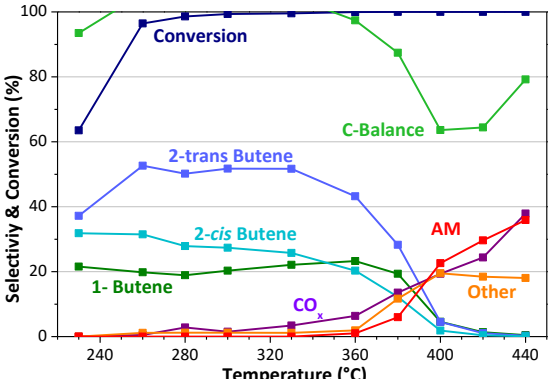


Figure 5: Effect of temperature on 1-butanol conversion and selectivity to products with the VPD catalyst. Feed composition: 1% butanol in air.

References

1. A. Chieregato et al. in *Chemicals and Fuels from Bio-Based Building Blocks (eds F. Cavani, S. Albonetti, F. Basile and A. Gandini)*, Wiley-VCH Verlag GmbH & Co. KGaA **2016**, pp. 1–32.
2. G. Pavarelli et al. *ChemSusChem*, **2015**, *8*, 2250–2259.
3. A. Chieregato et al. *Coord. Chem. Rev.*, **2014**, *301–302*, 3–23.

Antimicrobial release from s-PS Active Packaging

Cozzolino Antonietta[a], *Rizzo Paola*[a], *Guerra Gaetano*[a]

[a]*Dipartimento di Chimica e Biologia, INSTM Research Unit, Università di Salerno, Via Giovanni Paolo II 132, 84084,Fisciano (SA), Italy; e-mail:prizzo@unisa.it*

Active packaging is used successfully for improvement of shelf-life and nutritional quality of fresh food, especially processed ones, consumers need more and more high quality products that are also fresh and safe (1). Active packing is an innovative concept that can be defined as a packaging mode in which the bag, product and environment interact with each other in a synergistic way to extend shelf-life or enhance safety and sensory properties, while maintaining the quality of the product. This is particularly important in the fresh food sector, such as cut fruit (2). Semicrystalline s-PS samples, exhibiting thenanoporous δ and ε crystalline phases, can rapidly andselectively absorb volatile organic compounds as well as gasmolecules, even when present at very low concentrations (3).These s-PS films, mainly for low guest content(possibly <1 wt %) can be useful for packaging of fruits andvegetables, due to the combination of ethylene and carbondioxide removal from the empty cavities of the δ nanoporouscrystalline phase (4-6) and the slow release of a scented naturalantimicrobial guest from the filled cavities of the same crystallinephase (7).This slow release assures and hence long-term antimicrobialproperties (7).

Fig. 1. Orange fridge storage in BOPP film (left) and in sPS Activepackaging film (right) after 30 days.

References

1. T. P. Labuza, W. M. Breene, Applications of active packaging for improvement of shelf-life and nutritional quality of fresh and extended shelf-life foods, J Food Proc Preserv, 2008, 45, 1-9;
2. R. Ahvenainen, Active and intelligent packaging: an introduction, Woodhead Publishing Ltd, 2008, Cambridge, UK; 3. C. Manfredi, M. A. Del Nobile, G. Mensitieri, G. Guerra, M.Rapacciuolo, J. Polym. Sci., Polym. Phys. Ed. 1997, 35, 133-140;
3. A.R. Albunia, T. Minucci, G. Guerra, Ethylene removal by sorption from polymeric crystalline frameworks.Journal of Material Chemistry, 2008, 18, 1046-1050.
4. L. Annunziata, A.R. Albunia, V. Venditto, G. Mensitieri, G. Guerra, Polymer/Gas Clathrates for Gas Storage and Controlled Release. 2006, Macromolecules 39, 9166-9170.
5. V. Sicari, G. Dorato, A. M. Giuffre', P. Rizzo,A.R. Albunia, The effect of different packaging on physical and chemical properties of oranges during storageJ Food Process Preserv. 2017;e13168.
6. A. R. Albunia, P. Rizzo, G. Ianniello, C. Rufolo, G. Syndiotactic Polystyrene Films with a Cocrystalline Phase Including Carvacrol Guest Molecules, J. Polym Sci. 2014, 52, 657–66.

Biorefinery from the marine microalga Nannochloropsis oceanica

Antonella Salvini[a,c], Arianna Bracciali[a], Bernardo Grossi[a], Donatella Giomi[a,c], Mario Tredici[b,c], Liliana Rodolfi[b,c], Massimo D'Ottavio[b], Luca Meschisi[b], Alberto Brandi[a,c]

[a] Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI);
[b] DISPAA, Università degli Studi di Firenze, Piazzale delle Cascine, 24 - 50144 Firenze (FI);
[c] VALORE - Centro di competenza GINO FLORENZANO, Università degli Studi di Firenze; antonella.salvini@unifi.it

The exploitation of renewable materials coming from biomass is a strategic objective for the chemical industry in order to reduce the consumption of fossil resources resolving, at the same time, the problem of agricultural and other wastes disposal.The sustainability of a process is strongly dependent on the choice of raw materials able to produce high value derivatives or common productspreserving the availability of natural resources (especially for food supply) for the future generations. In this context, the valorization of biomass which production does not compete with food (wastes or microalgae) is an importantgoal. In this research project, extraction processes from algal biomass were studied for the optimization of biofuels production as well as the recovery of biomolecules to exploit in the pharmaceutical and nutraceutical domains or to develop high value products such as solvents, chemical industry intermediates and biopolymers.
Nannochloropsisoceanica biomass was provided by Fotosintetica & Microbiologica Srl (F&M), spin-off company of the University of Florence, within the activities of VALORE (Centro di Competenza *Gino Florenzano*of the University of Florence for the valorization of algal and residual biomasses). Improvement of extraction processes was studied in order to recover high value molecules for their industrial exploitation. In particular, the extraction process aimed at obtaining products with different applications: oils to obtain biodiesel and omega-3 fatty acids, carbohydrates or their derivativesable to be converted into other compounds of industrial interest and finally proteins for use in nutraceuticals.The main components extracted were characterized by NMR, FT-IR, GC-MS and CHN elemental analysis and synthetic processes were studied to transform some of these products in high value-added derivatives.
A combined microwave (MW)/Soxhlet method was chosen to extract high purity oil from *Nannochloropsis* biomass. In the Soxhlet extraction,petroleum ether was used as solvent with both oil poor and oil rich biomasses, with or without preliminary MW treatment. The best result in oil extraction (30% as w/w yield on a 55% total lipid content) was obtained using a lipid-rich biomass and MW/Soxhlet combined protocol. The ^{1}H-NMR analysis of the extracted oil revealed the presence of triglycerides with high purity and low amounts of other fatty acid derivatives. Polyunsaturated fatty acids (omega-3) were also detected and recovered as methyl esters by distillation in the biodiesel (BD) production. In fact, a mixture of fatty acid methyl esters was obtainedusing MeOH and TMSCl as a recyclable acidic mediator (8h, 60°C) and a conversion of 95% was evaluated via ^{1}H-NMR. This synthetic procedure was already applied for BD production from other biomasses (1-3).
Methyl-D-glucoside and cellulose derivatives were synthesized from the carbohydrate components and a protein enriched fraction was also recovered.

References

1. Brandi, A.; Salvini, A.; Cipriani, G.; Giomi, D.; Bartolozzi, G. *Process for the production of biodiesel by transesterification of triglycerides*, WO 2011023712 A1, **2011**.
2. Salvini, A.; Giomi, D.; Cipriani, G.; Bartolozzi, G.; Alfini, R.; Brandi, A. *RSC Adv.* **2012**, *2*, 4864-4868. 3. Malavolti, M.; Brandi, A.; Salvini, A.; Giomi, D. *RSC Adv.***2015**, *5*, 77341-77347.

Looking at the bigger picture in carbon dioxide photoreduction

Michela Signoretto[a], *Alberto Olivo*[a], *Maela Manzoli*[b], *Ilenia Rossetti*[c],*Mercedes Maroto-Valer*[d]
[a] *Dept. of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and Consortium INSTM, RU of Venice, Via Torino 155, 30172 Venezia, Italy;* [b] *Dept. of Drug Science and Technology & NIS Interdepartmental Centre, University of Turin, Via P. Giuria 7, 10125 Turin, Italy;* [c] *Dept.of Chemistry, University of Milan, INSTM Unit Milano Università and CNR-ISTM, via C. Golgi 19, 20133 Milan, Italy;*
[d]*Centre for Innovation in Carbon Capture and Storage (CICCS), Institute of Mechanical, Process and Energy Engineering (IMPEE), School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK;*
e-mail: miky@unive.it

CO_2 photocatalytic reduction, a growing field in green catalysis, shows great potentialities to avoid fossil fuels exploitation and to obtain C-based solar fuels through a sustainable process using water as a reductant and light irradiation as only energy input (1). Despite the simplicity of this reaction on paper, actually, there are several physical phaenomena and chemical side-reactions to be dealt with (2), but the two most critical are still carbon dioxide compatibility in reaction medium and light harvesting. In fact, reactants, catalyst (usually a TiO_2 based material) and light must all come together in order to successfully achieve effectiveness in carbon dioxide photoreduction. In this contribution, these parameters effects are considered carefully through a "catalysis by design" approach.Carbon dioxide compatibility toward water is extremely low and this issue still represents a challenge. To overcome this drawback, in this work the authors considered carbon dioxide photoreduction in different media, namely aqueous liquid phase and gas phase. It was observed that in liquid phase, where CO_2 absorption in water is less likely to happen, reaction occurs with a good yield only when reactor temperature and pressure are increased. Whereas, working in gas phase allows to perform the reaction at room temperature and atmospheric pressure and to modify products distribution to more reduced C-based products. CO_2 adsorption on the catalyst could be also tuned through catalyst modification, i.e. the introduction of basic components (such as CaO or MgO) on the catalytic surface, though these promoters modify the chemical properties of adsorbed carboxyl-species with different reducibilities, as indicated by physicochemical characterisations.
Carbon dioxide adsorption aside, light harvesting on photocatalyst can be increased by materials modification. Enhanced electronic circulation on semiconductive materials by metal doping boosts the effectiveness of incident photons. In this work, the effects of CuO (a co-catalyst) and Au (an electron trap) is carefully considered to reduce electron-hole recombination in titanium dioxide. While CuO increased both activity and selectivity to methane, surprisingly gold suppressed methane formation in favour of hydrogen due to water splitting side-reaction. A deep physicochemical characterisation allowed to correlate this experimental data to materials' properties: in fact, from FTIR data, it was possible to observe that gold nanoparticles acts as a too strong trap for electrons preventing them from remaining in titanium dioxide's conduction band and being photocatalytically active. Finally, CO_2photoreduction to methane in both photons-rich and photons-poor conditions, in order to assess the effect of the promoters on light harvesting in different experimental regimes. In all conditions CuO and Au modified TiO_2 photoactivity, but this difference was more evident in low irradiance conditions, where light harvesting takes on great importance. From all the experimental evidences and considerations, there is a wide variety of pursuable strategies to increase carbon dioxide photoreduction efficiency, but they must be carefully considered by an in-depth consideration of physical and chemical phenomena involved in the process.

References:

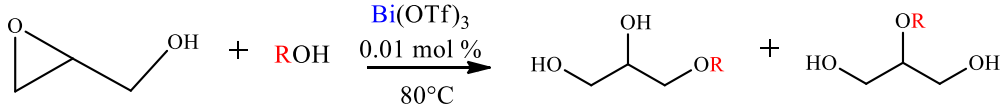
1. O. Ola, M. Maroto-Valer, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 24 (2015) 16-42.
2. A. Olivo, V. Trevisan, E. Ghedini, F. Pinna, C.L. Bianchi, A. Naldoni, M. Signoretto, Journal of CO_2 Utilization 12 (2015) 86-94.

Synthesis of monoalkyl glyceryl ethers using glycidol as green starting material

Maria Ricciardi[a], *Raffaele Cucciniello*[a], *Daniele Cespi*[b], *Carmine Capacchione*[a], *Ivano Vassura*[b], *Fabrizio Passarini*[b], *Antonio Proto*[a]

[a] *Department of Chemistry and Biology "Adolfo Zambelli" University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy;*
[b] *Department of Industrial Chemistry "Toso Montanari'' University of Bologna, Viale del Risorgimento 4, 40135 Bologna, Italy; mricciardi@unisa.it*

The present work deals with the selective preparation of monoalkyl glyceryl ethers (MAGEs) starting from glycidol (2,3-epoxy-1-propanol) by ring opening reaction with alcohols.
MAGEs are a versatile class of chemical compoundswith several industrial applications, in particular theyare used as the building blocks for the production of additives (for fuels,lubricants, printing inks etc.), detergents, polymers, pharmaceutical and cosmetic products.(1)
One of the most investigated pathway to synthesize MAGEs is represented by the direct etherification of glycerol,thanks to thegreat abundance of this feedstock on the market (2.3 Mt in 2013).
The use of glycidolas starting material to produce such valuable chemicals appears to be very promising if we considerthat it can be obtainedthrough the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant. (2)
We have studied the catalytic etherification of glycidol with alcohols in the presence of Lewis acids and we have obtained the best results by using metal triflates as catalysts. (3)
In this work, we explore the synthesis of MAGEs catalyzed by an environmental friendly Lewis acidscatalyst, such as $Bi(OTf)_3$ (Scheme 1), which is recognized asthe best catalyst for the synthesis of monobutoxy glyceryl ethers starting from glycerol.



R= CH_3, CH_2CH_3, $CH(CH_3)_2$, $(CH_2)_3CH_3$, $(CH_2)_4CH_3$, $(CH_2)_7CH_3$, CH_2Ph.

Scheme 1. Glycidol etherification with alcohols in the presence of bismuth triflate.

Under the investigated reaction conditions, $Bi(OTf)_3$ was shown to promote the total conversion of glycidol with high selectivity (90%) to monobutoxy glyceryl ethers in only 2 h.
A simplified life cycle approach was followed by comparing thesustainabilityof the proposed route with that of the most investigated pathway from glycerol, in order to evaluate the green potentialof MAGEs synthesis from glycidol.The results showa considerable reduction of all the impact categories considered, suggesting that the glycidol-to-MAGEs route can be a valuable integration to the glycerol-to-MAGEs chain. (4)

References

1. Sutter, M.; Silva, E. D.; Duguet, N.; Raoul, Y.; Métay, E.; Lemaire, M. *Chem. Rev.***2015**, *115*, 8609-8651.
2. Cespi, D.; Cucciniello, R.; Ricciardi, M.; Capacchione, C.; Vassura, I.; Passarini, F., Proto, A. *Green Chem.***2016**, *18*, 4559-4570.
3. Cucciniello, R.; Ricciardi, M.; Vitiello, R.; Di Serio, M.; Proto, A., Capacchione, C.; *ChemSusChem***2016**, *9*, 3272–3275.
4. Ricciardi, M.; Passarini, F.; Vassura, I.; Proto, A.; Capacchione, C., Cucciniello, R., Cespi D. *ChemSusChem***2017**, *10*, 2291 –2300.

Comunicazioni Poster

Titanium grids and polymer electrolytes for flexible dye-sensitized solar cells

Federico Bella[a], *Alberto Scalia*[a], *Matteo Gerosa*[a], *Adriano Sacco*[b], *Stefano Bianco*[a], *Marzia Quaglio*[b], *Angelica Chiodoni*[b], *Elena Tresso*[a], *Candido F. Pirri*[a]

[a] *Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Torino, Italy;*
[b] *Center for Sustainable Future Technologies @Polito, Istituto Italiano di Tecnologia, Corso Trento 21, 10129-Torino, Italy;*
e-mail: *federico.bella@polito.it*

Dye-sensitized solar cells (DSSCs) gather great interest for the possibility of different applications such as architectural integration, wearable photovoltaics and supply systems for low power electronics. For the development of flexible devices some critical issues still have to be solved, such as the use of solid or quasi-solid electrolytes and convenient sealing materials for the packaging, able to provide satisfactory duration in time.
This work presents the results obtained on a flexible DSSC, fabricated in our lab using UV-crosslinked polymeric membrane as electrolyte and titanium grids both as the anode andas the cathode substrate. The Ti grid was vertically dipped into a diluted TiO_2 paste (18NR-AO ActiveOpaque, Dyesol), in order to obtain a suitable mesoporous semiconductive layer, which was subsequently annealed at 525 °C. The photoanode was then incubated into a 0.3 mM N719 dye solution (Ruthenizer535bis-TBA, Solaronix) for 15 h. The cathode was obtained depositing a 5 nm layer of platinum by means of sputtering (1). Regarding the polymeric membrane, this was prepared UV-irradiating a solution of two oligomers (bisphenol A ethoxylate dimethacrylate, BEMA and poly(ethylene glycol) methyl ether methacrylate, PEGMA) and a free-radical photoinitiator (2). The packaging was made with two 75µm-thick PET foils and each layer of the cell was spaced by a thermoplastic foil. The sealing was performed using a hot press set at 85 °C.
Both rigid and flexible DSSC configurations have been tested by a careful characterization of their electrical performances. The small decrease in the overall efficiency of the flexibleDSSC configuration with respect to the rigid one is related to the different quality of the electrodes/electrolyte interface contacts.
In conclusion, the simplicity of fabrication and the relatively low cost employed materials pave the way for an industrial scale-up and a possible future commercialization.

References

1. M. Gerosa, A. Sacco, A. Scalia, F. Bella, A. Chiodoni, M. Quaglio, E. Tresso and S. Bianco, *IEEE J. Photovoltaics***6** (2016) 498-505.
2. F. Bella, A. Lamberti, A. Sacco, S. Bianco, A. Chiodoni and R. Bongiovanni, *J. Membr. Sci.***470** (2014) 125-131.

Bioadditives from waste materials

Arianna Bracciali[a], *Antonella Salvini*[a], *Donatella Giomi*[a], *Alberto Brandi*[a]

[a]*Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia, 3-13 - 50019 - Sesto Fiorentino, Italia; ariannabracciali@alice.it*

Recycling and reprocessing of waste materials to obtain bioadditives, biopolymers or biodiesel (BD) is becoming a primary topic for biorefinery productions. In fact, in a world wide scale production, with different economic, political, environmental and ethical issues, many efforts have been made to convert non-ediblefeedstocksuch as non-edible oils, exhausted fried oils, oils from microalgae, animal fats and other waste materials into chemicals or biofuels. A preliminary study has been performed in order to obtain bioadditives with different reagents potentially achievable from a biorefinery, with the aim to identify the major transformation products and their industrial applications. In particular, due to the complexity of the mixtures obtained from substrate as glycerol or sugars, ethylene glycol was used as a model compound to optimize selectivity and conversions in the esterification with oleic acid usingchlorotrimethylsilane (TMSCl) as a recyclable acidic mediator. In fact, this compound was already applied for the transesterification of triglycerides to obtain BD (1-3) and also for the chlorination of glycerol to obtain mono and dichlorohydrins (4). The use of ethylene glycol is interesting for the valorization of this product after its recovery from waste materials coming from the demolition of cars.Three products were obtained from the reaction between oleic acid and ethylene glycol(Figure 1).

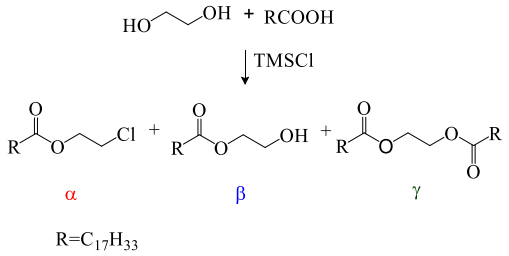


Figure 1. Synthesis of oleic acid derivatives

The selectivity can be changed modifying the molar ratio between the reagents or the temperature and in particular compound αor β were obtained with high selectivity using different reaction conditions. Product α could be used for the synthesis of a cationic biosurfactant, while β and γ could be used as surfactant and as plasticizer, respectively. Work up procedure was optimized to recover and recycle unconverted ethylene glycol and oleic acid.

References

1. Brandi, A.; Salvini, A.; Cipriani, G.; Giomi, D.; Bartolozzi, G. *Process for the production of biodiesel by transesterification of triglycerides*, WO 2011023712 A1, **2011**.
2. Salvini, A.; Giomi, D.; Cipriani, G.; Bartolozzi, G.; Alfini, R.; Brandi, A. *RSC Adv.* **2012**, *2*, 4864-4868.
3. Malavolti, M.; Brandi, A.; Salvini, A.; Giomi, D. *RSC Adv.***2015**, *5*, 77341-77347.
4. Giomi, D.; Malavolti, M.; Piccolo, O.; Salvini, A.; Brandi, A. *RSC Adv*, **2014**, *4*, 46319-46326.

The reactivity of metal phosphate catalysts in the synthesis of methyl methacrylate from bio-based propionic acid and methanol

Jacopo De Maron[a], *Claudia Bandinelli*[a], *Francesco Basile*[a], *Fabrizio Cavani*[a]

[a]*Dipartimento di Chimica Industriale,Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy; e-mail:jacopo.demaron2@unibo.it*

Poly(methyl methacrylate) (PMMA) is a plastic material widely used by automotive, construction, electronics and display industries. Most methyl methacrylate (MMA) produced globally is employed in the manufacturing of PMMA, but so far MMA synthesis almost relies on oil-derived chemicals such as acetone, ethylene, propylene and isobutene (1). Among the renewable resources available for MMA synthesis, an interesting option would be propionic acid (PA), which can be produced either by sugars or by glycerol fermentations (2), or by dehydration and oxidation of 1,2-propanediol. Here we report a study on the direct synthesis of MMA and methacrylic acid (MA) in the gas phase in a fixed-bed continuous-flow reactor, by means of esterification of PA with MeOH and aldol condensation between PA and formaldehyde (the latter produced in-situ by MeOH dehydrogenation). Amorphous Al phosphate proved to be effective in the esterification of PA giving good selectivities in methyl propionate (MP), namely 72%, with a time factor of 1 s*g/mL. However,in the range of temperature investigated (300-350-400°C), this catalyst yielded MMA and MA with overall selectivity no higher than 8%, because of the expected poor catalyst activity in methanol dehydrogenation to formaldehyde, and the need for a dehydrogenating element such as Cu or Ag.Surprisingly, at high temperatures (400°C), 3-pentanone (3-P) became a major product of the reaction with a selectivity of 20%. The ketonic decarboxylation of carboxylic acids has been studied extensively on basic and transition metals oxides (3) but, to the best of our knowledge, there are very few literature references on the use of metal phosphates as catalysts for ketonization of carboxylic acids.Since bio-oil produced from ligno-cellulose pyrolysis contains carboxylic acids and this leads to low pH, instability and corrosiveness, ketonization would be a viable option to remove contaminants and enhance the quality of bio-fuels (3). For these reasons, the self-ketonization of PA over amorphous Al phosphate and Zr phosphate has been investigated as well. When PA was fed over $AlPO_4$ in the range of temperatures 300-375 °C, the conversion rose from 12% to 83% and the major products was 3-P, with selectivity around 70%, the remaining however being mainly due to the CO_2 co-produced. Selectivity of 3-P was lower than that which would occur in the absence of consecutive reactions (83%) due to self-condensation, which formed heavy products on catalyst and reactor's walls. Rising temperatures to 400°C enhanced this side reaction lowering 3P selectivity down to 55%. The activity of Zr phosphate was lower than that of Al phosphate: the conversion of PA at 350 °C was 19% and rose to 53% when temperature was increased until 425 °C, while the trend of 3-P selectivity was similar to that obtained with Al phosphate.

References

1. K. Nagai, Appl. Cat. A: General, 2001, 221 (1-2), 367-377.
2. E. H. Himmi et al, Appl. Microbiol. Biotechnol., 2000, 53 (4), 435-440.
3. T. N. Pham et al, ACS Catal., 2013, 3 (11), 2456-2473.

Alumina-supported niobia catalystsfor methylesters epoxidation reaction

Martino Di Serio[a], Rosa Turco[a], Rosa Vitiello[a], Vincenzo Russo[a], Riccardo Tesser[a]

[a] University of Naples Federico II, Department of Chemical Sciences, Complesso Universitario di Monte Sant'Angelo, 80126 Naples, Italy; martino.diserio@unina.it

Epoxidized soybean oil and epoxidized methylesters derived by oils play an important role as building blocks for the preparation of a wide variety of consumer products, such as plasticizers and stabilizers for PVC, and components of lubricants. On the industrial scale, the epoxidation reaction is currently carried out with peroxocarboxylic acids, obtained in situ by using mineral acids as catalysts according with the Prileshajew method. However, several drawbacks of this method have been recognized over the years, such as the occurring of side reactions (ring opening and polymerization) caused by the presence of homogeneous acids in the reaction system, and the environmental pollution of the waste acids [1]. New efficient and environmentally friendly systems, such as the use of alternative oxidants and heterogeneous catalysts, may overcome these limitations. In particular, the use of hydrogen peroxide as oxidant is very attractive because the only one by-product of the reaction is water.
Recently, many niobium oxide (niobia) based materials (Nb_2O_5/SiO_2) were proposed for the epoxidation reaction with hydrogen peroxide, due to the high leaching stability and good water tolerance. In particular, it was demonstrated that the niobia–silica based materials, containing the same amount of Nb_2O_5 and prepared by different synthesis methods, have different catalytic activity in methyloleate epoxidation with H_2O_2 [2,3]. This singular behavior was ascribed to the presence of different species of niobium (isolated or bulk) depending on the nature of the niobium precursor and the synthesis method. Different methods of synthesis lead to the presence of different structures and surface distribution of active sites (Brønsted and Lewis sites), influencing in this way the activity and selectivity in the epoxidation reaction. Commercial alumina was reported as an efficient catalyst for the epoxidation of methyloleate with hydrogen peroxide, also in the presence of a large substrate like soybean oil [4] moreover it has recently been demonstrated that catalysts obtained supporting Nb_2O_5on alumina are very good catalyst with high activity and selectivity [5].
The aim of this work is to study deeper the catalytic system (Nb_2O_5/Al_2O_3). In particular, the influence of the preparation conditions on catalyst structure and on catalytic performance will be examined.

References

1. R. Turco, R. Vitiello, V. Russo, R. Tesser, E. Santacesaria, M. Di Serio, *Green Proces. and Synth.*, 2, (2013) 427.
2. A. Feliczak, K. Walzak, A, Wawrzynczak, I. Novak, *Cat Today*, 140, (2009) 23.
3. R. Turco, A. Aronne, P. Carniti, A. Gervasini, L. Minieri, P. Pernice, R. Tesser, R. Vitiello, M. Di Serio, Cat. Today, 254, (2015) 99.
4. R. Turco, C. Pischetola, R. Tesser, S. Andini, M. Di Serio, RSC Adv., 6, (2016) 31647.
5. R. Turco, R., R.Vitiello, R.Tesser, A. Vergara, S. Andini, M. Di Serio Top Catal (2017). doi:10.1007/s11244-017-0808-y.

Epoxidation of methyl oleate with hydrogen peroxide as oxidizing agent over niobium and titanium oxide-based catalysts

Matteo Guidotti[a], *Nicoletta Ravasio*[a], *Claudio Evangelisti*[a], *Rinaldo Psaro*[a], *Prashant Niphadkar*[b], *Vijay Bokade*[b]

[a] *CNR-Istituto di Scienze e Tecnologie Molecolari, Milano, Italy*
[b] *CSIR-National Chemical Laboratory, Pune, India*
m.guidotti@istm.cnr.it

Epoxidised vegetable oil fatty acid methyl esters (FAMEs) are considered among the most versatile intermediate materials for oleochemistry, as they may give rise to a broad palette of valuable derivatives via epoxide ring opening (1). Niobium- and titanium-based silica catalysts proved to be promising heterogeneous catalysts able to promote the use of aqueous hydrogen peroxide as an eco-friendly oxidant in epoxidation reactions (2,3). Since several literature reports rely on the use of chemically complex, non-commercial solid catalysts, that are scarcely suitable for a large-scale application, the present study aimed at investigating the performance of conceptually simple, cost effective inorganic oxides to be used in the liquid-phase epoxidation of methyl oleate (Me-OLE), as a model substrate, in the presence of aqueous (30 wt.%) hydrogen peroxide.
Commercially-available samples of nanometric-sized $Nb_2O_5 \cdot 5H_2O$, anatase $TiO_2$and SiO_2-TiO_2 mixed oxides (with TiO_2 content spanning from 0.3 to 2.3 wt.%) were chosen as catalysts. The materials underwent a thorough physico-chemical characterization (XRD, DRS-UV-vis and SEM). Only the SiO_2-TiO_2 0.3% sample displayed a major fraction of isolated Ti(IV), whereas in the rest of the materials the presence of bulky aggregates of TiO_2 or Nb_2O_5 species was clearly evident.
In batch epoxidation tests (Fig. 1), under non-optimized conditions, $Nb_2O_5 \cdot 5H_2O$ showed the highest performance in terms of Me-OLE conversion (43%) and epoxide selectivity (54%) and yield (23%). A TS-1 zeotype (Ti content 1.7%), taken as a benchmark catalyst, was more selective (71%), albeit at the cost of lower conversion values (down to 14%) due to its narrow and poorly accessible micropore network. The encouraging results obtained on $Nb_2O_5 \cdot 5H_2O$ and its intrinsic structural robustness in water-containing media are feature worth studying in deeper detail.

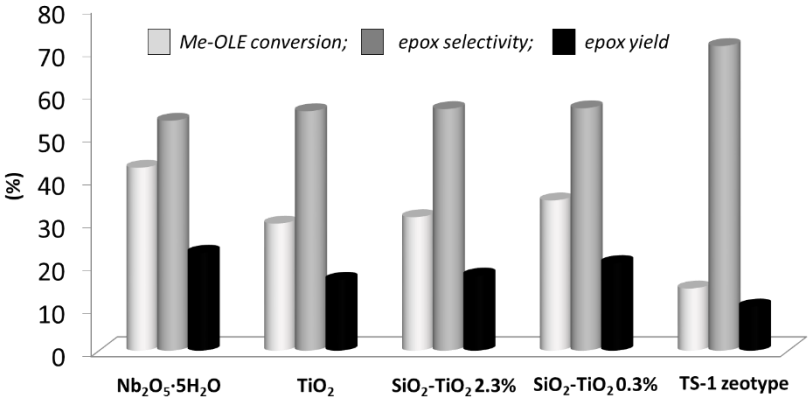


Fig. 1. Catalytic performance of the oxidic heterogeneous catalysts in the batch liquid-phase epoxidation of methyl oleate. Reaction conditions: H_2O_2:Me-OLE 4:1 mol/mol; 0.7g solid; 3 g CH_3CN; 90°C; 4h.

ISTM and NCL gratefully acknowledge the CNR, Italy – CSIR, India Bilateral Programme "Development of Catalytic Renewable Process by Converting Indian Origin Non-Edible Oil to Valuable Chemicals" for partial financial support.

References

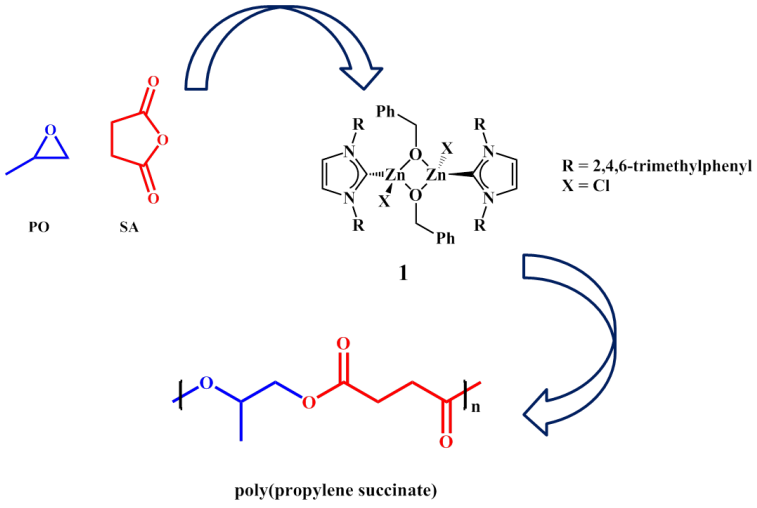
1. Guidotti, M., Palumbo, C., in: Atwood, D.A. (Ed.), Encyclopedia of Inorganic and Bioinorganic Chemistry. (2016) J. Wiley & S., Chichester, UK, pp. 373–385.
2. Guidotti, M., Psaro, R., Ravasio, N., Sgobba, M., Gianotti, E., Grinberg, S., Catal. Lett. 122 (2008) 53.
3. Tiozzo, C., Bisio, C., Carniato, F., Marchese, L., Gallo, A., Ravasio, N., Psaro, R., Guidotti, M., Eur. J. Lipid Sci. Technol. 115 (2013) 86.

Copolymerization of Propylene Oxide with Succinic Anhydride using Dinuclear Zinc-*N*-heterocyclic carbene complexes

Rosita Lapenta[a], *Stefano Milione*[a],*Alfonso Grassi*[a],*Samuel Dagorne*[b]

[a]*Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 132 Fisciano, I-84084 Salerno (Italy);*
[b]*Institut de Chimie de Strasbourg, CNRS-Université de Strasbourg, UMR 7177, 1 rue Blaise Pascal, 67000 Strasbourg (France);rlapenta@unisa.it*

The growing demand for biodegradable polymers as alternative materials to conventional polyolefins requires the sustainable production of new materials, preferentially using monomers from renewable resources (1). In recent years, much attention has been being paid to aliphatic polyesters due to their biodegradability and biocompatibility (2): the latter include materials such as polylactide (PLA), poly(ε-caprolactone) (PCL) and, more recently, copolymers like poly(propylene succinate) (PPSu) and poly(cyclohexene succinate) (PCSu). PPSu and PCSu are polyesters of potential interest for application in the drug delivery agents, as fibers and medical sutures/stents (3). These copolymers can be produced in a controlled manner by ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides, typically mediated by complexes of oxophilic metals, such as group 13 M(III) and Zn (II) (4). Zn(II)–alkoxide species are particularly attractive metal-based ROP initiators because of the low cost and low toxicity of Zn. Besides, Zn(II) species are well-established catalysts for the effective and controlled homo-polymerization of various cyclic esters/carbonates. However, the use of Zn-based initiators for the epoxide/anhydride ROCOP remain little studied so far. Herein a series of robust zinc complexes bearing monodentate N-heterocyclic carbenes (NHCs), synthetized according to a literature procedure (5), were investigated as initiators of the copolymerization of propylene oxide (PO) with succinic anhydride (SA). The present contribution describesour preliminary results in the area under different reaction conditions. Complex **1** was found to be an active ROCOP catalyst leading to good polymerization control and activity.



References

1. Williams, C. K.; Hillmyer, M. A *Polym. Rev.***2008**, *48*, 1.
2. Albertsson, A. C.; Varma, I. K. *Biomacromolecules*, **2003**, *4*, 1466.
3. Longo, J. M.; Sanford, M. J.; Coates, G. W. *Chem. Rev.***2016**, *116*, 15167−15197.
4. Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. *Chem. Commun*., **2015**, *51*, 6459.
5. Jensen, T. R.; Schaller, C. P.; Hillmyer, M. A.; Tolman, W. B. *J. Organomet. Chem.*, **2005**, *690*, 5881.

Hydrogen production by ethanol steam reforming on Ni-based catalysts: effects of the support and of CaO and Au doping

Federica Menegazzo[a], *Cristina Pizzolitto*[a], *Michela Signoretto*[a], *Alessandro di Michele*[b], *Cas Buysschaert*[c]

[a]*Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM RU of Venice, via Torino 155, 30172 Venezia Mestre, Italy;*
[b]*Physics and Geology Department, University of Perugia, Via Pascoli, 06123 Perugia, Italy;*
[c]*Chemical Engineering, Faculty of Engineering Technology, Campus Group T Leuven 13, 3000 Leuven, Belgium;*
e-mail fmenegaz@unive.it

Energy is everywhere. Energy is the base for social and economic development, and it represents a necessity for everyday life.One of the main challenge for scientists today is to reduce the dependence from fossil fuels. However, how can we meet the ever-growing world energy demand in a sustainable way?Renewables can be the answer (1). Hydrogen and renewables-derived hydrogen in particular, is the ideal candidate for both energy and transport sectors. It is a high-density energy vector; it is clean and carbon-free, so its sole combustion product is water. Ethanol emerged as a good candidate for hydrogen production because it is renewable, easy to store, handle and transport because of its low volatility and non-toxicity and has a high hydrogen content. Therefore, ethanol steam reforming (ESR) is promising to produce hydrogen in a sustainable way.

The aim of the present work is the development of Ni based catalysts for hydrogen production by ESR. As the choice of the support plays a vital role in determining the activity, selectivity and stability of a catalyst, we have studied three different metal oxides: titania, zirconia and ceria. In particular, we have investigated 10 wt% supported Ni samples with the addition of calcium oxide (9 wt%) by incipient wetness impregnation and of a small amount of gold (1wt%) by deposition precipitation. As regard as the active phase, nickel is extremely attractive to upscale the process for one reason: the price. Nickel showed a high activity and efficiency in breaking the C-C bond but its use is limited by coking and sintering phenomena. Noble metals are known for their ability to break the C-C bond and it is known that gold nanoparticles favor the water gas-shift reaction as well. Moreover, calcium oxide was added to the supports in order to reduce the acidity of the catalysts and prevent coke formation (2).

Both fresh and used samples were properly characterized to understand the influence of the dopants on morphological, textural and surface properties by N_2-physisorption, XRD, TPR, TPO, CO_2-TPD, SEM, AAS and IC. The evaluation of the catalytic performances in the ESR were proved in a plug-flow reactor PID (Process Integral Development Eng&Tech) coupled to a gas-chromatograph and to quadrupole mass analyzer.

It was found that the support plays a very important role on nickel activity in ESR.Zirconium and cerium oxides proved to be suitable supports, even if both still suffer from coking phenomena.

Doping by calcium oxide prevented deactivation and highly increased the hydrogen yield and productivity. The resistance towards coking increased due to the formation of oxygen vacancies, that can activate CO_2 and H_2O, thus favouring the gasification of coke.

Addition of gold nanoparticles greatly improved the hydrogen yield.

The combination of the two dopants resulted in the best performing catalyst: the basic doping by CaO and the promotion of the WGS by gold nanoparticles contributed to the highest hydrogen production.

References

1. Y. D. Goswami, F. Kreith, Energy efficiency and renewable energy handbook, second edition, CRC press, London, 2015.
2. V. Nichele, M. Signoretto, F. Pinna, F. Menegazzo, I. Rossetti, G. Cruciani, G. Cerrato, A. Di Michele, Applied Catalysis B: Environmental, 150-151 (2014) 12-20.

A new Material for Digital Doming: Preparation of Polyurethanes based on Soybean Oil

Vincenzo Pantone[a], *Amelita G. Laurenza*[b], *Cosimo Annese*[c], *Michele Casiello*[b], *Roberto Comparelli*[d], *Paola Fini*[d], *Caterina Fusco*[c], *Angelo Nacci*[b,c], *Antonella Russo*[a], *Lucia D'Accolti*[b,c]

[a]*Greenswitch s.r.l., Ferrandina (MT), Italy;*
[b] *Dipartimento di Chimica, Università di Bari "A. Moro", Via Orabona 4, 70126 Bari, Italy;*
[c]*ICCOM-CNR, SS Bari, Via Orabona 4, 70126 Bari, Italy;*
[d]*IPCF-CNR, SS Bari, via E. Orabona 4, 70125 Bari, Italy. vincenzo.pantone@greenswitch.it*

Most of the worldwide market plastics derive from fossil fuels such as oil, coal and natural gas, accounting for about 7% of world consumption of these resources. Considering the continuous depletion of fossil raw materials, the oil price fluctuations and environmental problems, in the last decade a wide-ranging research started on the production of "bio-based" polymeric materials coming directly or indirectly from renewable raw materials such as starch, cellulose, sugars, lignin, etc. (1) In this context, vegetable oils, such as castor, linseed, and soybean oils, have been regarded as a convenient renewable feedstock for developing bio-based polyurethanes. (2) In our previous work, we reported an efficient, cost-effective, and environmentally-safer conversion of soybean oil (SO) into soy-based PU, (fig. 1A) (3).A special application of PU is the digital doming, a process which adds value to any shape or size non porous material by coating the surface with a thick layer of resin (up to 5 mm) having a dome shape, that is due to the high surface tension of the liquid polymer during solidification. This technique gives to the surface a three-dimensional effect (fig.1B).

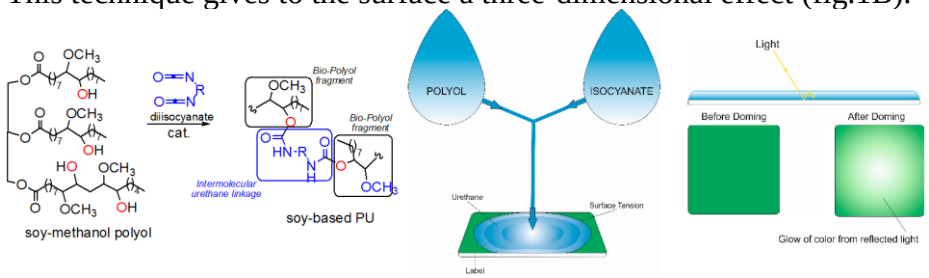


Figure 1. (A)Soy-methanol polyol and PUs, (B) Example of Doming Effect

We now report a new formulation to obtain e Bio-based Polyurethane for innovative application in Digital Mosaics. (fig. 2)

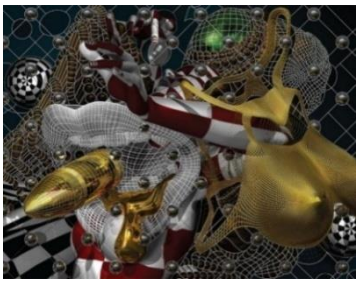


Figure 2. An example of Digital Mosaic in Erarta Museum

References

1. Li, X. Luo, S. Hu, Bio-based Polyols and Polyurethanes Springer Cham Heidelberg New York Dordrecht London, 2015. DOI 10.1007/978-3-319-21539-6
2. Z. S. Petrovic Polyurethanes from Vegetable Oils Polym Rev. 48 (2008) 109-155.
3. V. Pantone, C. Annese, C. Fusco, P. Fini, A. Nacci, A. Russo, L. D'Accolti One-Pot Conversion of Epoxidized Soybean Oil (ESO) into Soy-Based Polyurethanes by MoCl2O2 Catalysis. Molecules 22 (2017) 333-346. doi:10.3390/molecules22020333.

Methane dry reforming: effects of lanthanum oxide in Ni/CeO_2 catalyst

Cristina Pizzolitto[a], *Michela Signoretto*[a], *Federica Menegazzo*[a], *Danny Zanardo*[a], *Giuseppe Cruciani*[b]

[a] *Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM RU of Venice, via Torino 155, 30172 Venezia Mestre, Italy*
[b]*Department of Earth Sciences, University of Ferrara, via Saragat 1, I- 44100, Ferrara, Italy*

Nowadays the world is facing a big issue regarding the environmental problems represented by the use of fossil fuels as energy source. In fact, great emissions of CO_2, derived from fossil fuels combustion, and uncombusted methane have been responsible for the steep growth of the global mean temperatures, i.e. the so-called greenhouse effect.
In this work, methane dry reforming (MDR) is investigated in order to valorise methane and carbon dioxide, two of the greatest greenhouse gasses. *Syngas* in a low H_2/CO ratio is the product of this reaction and it's possible to exploit it in Fisher-Tropsh liquid hydrocarbons synthesis. The goal of the work is the formulation of a heterogeneous nanostructured catalyst based on nickel for MDR. Nickel is very active for this reaction but it suffers from deactivation caused by sintering and coke deposition (1). For this reason, it's necessary to increase its stability and resistance using supports with high surface area and thermal stability. Ceria was selected for its redox properties(2) that allow the storage and delivery of oxygen thanks to the reversible change of oxidation state from 3+ to 4+. Conversely, it has limited mechanical strength. For this reason, it was used lanthanum oxide as a promoter, in order to enhance the stability and the redox properties of this system. Aimed at optimising support-promoter interaction and maximise their synergistic effect, the synthetic method has been studied. Lanthanum oxide (6 wt %), was introduced on ceria support by two different methods: incipient wetness impregnation into the support and co-precipitation with the support. Reactivity tests were performed in a lab made reactor rig(3), controlling the products by an online mass spectrometer. Different techniques were used to characterise the samples: temperature programmed reduction (TPR), temperature programmed oxidation (TPO), X-Ray diffraction (XRD) and physisorption. In this way, it was seen how the support influences nickel particles size and interactions with the active phase, and the direct effect of these properties on the activity and stability of the catalyst for *syngas* production. It was observed an increase in hydrogen production after lanthanum oxide addition, but at the same time the activity was strongly affected by the promoter introduction method. XRD analysis have been essential in order to understand the reason of this behaviour. It has been observed an increment in lattice parameter with the addition of the promoter. In particular, co-precipitation method provides materials characterised by larger lattice parameter cell than impregnation method, proving former method's greater effectiveness in entering ceria lattice; in fact, La^{3+} and Ce^{4+} have similar -ionic radii. This feature therefore has a direct effect on catalytic performances. It is possible to suppose that the substitution of Ce^{4+} with La^{3+} in ceria lattice leads to a higher redox ability that decreased catalytic deactivation due to carbon deposition, and brought higher methane conversion.
Therefore, a proper lanthanum oxide modification on Ni/CeO_2 catalyst represents an efficient and innovative method to increase both activity and stability for MDR.

References

1. Z. Liu, S. D. Senanayake, J. A. Rodrigues; Applied Catalysis B: Environmental, 197 (2016) 184-197.
2. C.G. Rotaru, G. Postole, M. Florea, F. Matei-Rutkovska, V.I. Parvulescu, P. Gelin; Applied Catalysis A: General, 494 (2015) 29-40.
3. F. Menegazzo, M. Signoretto, F. Pinna, P. Canton, N. Pernicone Applied Catalysis A: General, 439-440 (2012) 80-87.

Photonic Crystal Sensors based on Poly(p-Phenylene Oxide)

Paola Rizzo[a], *Gaetano Guerra*[a], *Paola Lova*[b,c], *Chiara Bastianini*[b], *Maddalena Patrini*[d], *Mario Iodice*[e], *Cesare Soci*[c], *Davide Comoretto*[b]

[a]*Dip. di Chimica e Biologia, and INSTM Research Unit, Univ.di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy;*
[b.]*Dip. di Chimica e Chimica Industriale, Univ.di Genova, Genova (I);*
[c] *Centre for Disruptive Photonic Technologies, Nanyang Tech. Univ., Singapore;*
[d] *Dip.di Fisica, Univ. di Pavia, Pavia (I);*
[e] *Istituto per la Microelettronica e Microsistemi, C.N.R. 95121 Napoli, Italy;*
e-mail:prizzo@unisa.it

1D polymer photonic crystals, based on of poly(phenylene-oxide)(PPO), both in amorphous and clathrate crystalline phases, have been prepared.
The diffusion of certain molecules (VOC vapors) within amorphous PPO induces the formation of cocrystalline phases where guest molecules are included within the polymer lattice (1-6).
During exposure to the different VOCs, the DBRs (distributed Bragg reflectors) show a very dissimilar optical behavior, also detectable by naked eye. We have demonstrated a proof-of-concept all-polymer DBR sensor able to distinguishing benzene, 1,2-dichlorobenzene, carbon tetrachloride and toluene via colorimetric detection (7).
The visual colorimetric response of the sensor, which does not require any signal transduction, could potentially make these systems effective safety devices suitable for untrained end-users for monitoring of air quality and of VOCs leakages, also allowing constant and extensive pollution monitoring in industrial and urban areas

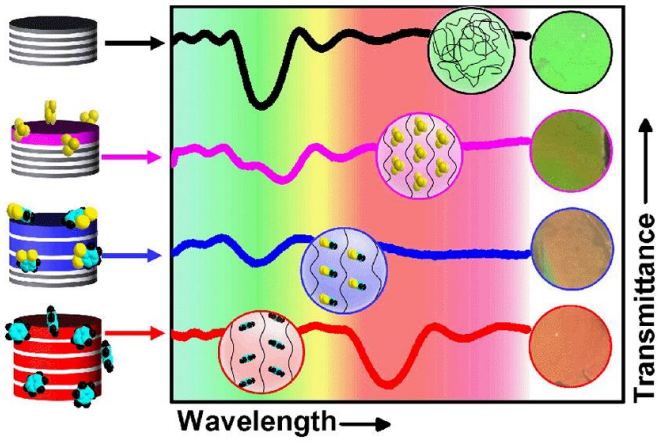


Fig. 1. A visual colorimetric response of a Photonic Crystal Sensors based on Poly(p-Phenylene Oxide) during exposure to VOC vapours

References

1. J. Ge and Y. Yin, Angew. Chem. Int. Ed., 50, 1492, 2011.
2. J. H. Moon and S. Yang, Chem. Rev., 110, 547, 2010.
3. G. Canazza, et.al Laser Phys. Lett., 11, 035804, 2014.
4. C. Daniel, S. Longo, G. Fasano, J.G. Vitillo, and G. Guerra, Chem. Mater. 23, 3195, 2011.
5. C. Daniel, S. Longo, G. Fasano, J.G. Vitillo, and G. Guerra, Chem. Mater. 23, 3195, 2011.
6. P. Rizzo, G. Ianniello, S. Longo, G. Guerra Macromolecules, 46, 3995,2013.
7. P. Lova, C. Bastianini, P. Giusto, M. Patrini, P. Rizzo, G. Guerra, M. Iodice, C. Soci, D. Comoretto ACS Appl. Mater. Interfaces, 8, 31941, 2016.

Crystalline orientation in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) cast films

Paola Rizzo[a],*Vissia Vitale*[a]

[a]*Dipartimento di Chimica e Biologia, and INSTM Research Unit, Univ.di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy; e-mail: prizzo@unisa.it*

The properties of polymeric films largely depend on the type and degree of molecular orientation developed during the processing or during the crystallization process, therefore it is very important to study and control the molecular orientations that can be generated in polymeric films (1).
It was found that polymers, which are able to form co-crystalline phases with low molecular mass molecules, can lead *without any stretching procedure* to high degrees of different kinds of uniplanar orientations of the crystalline phases, i.e., a high degree of parallelism of well defined crystal planes with respect to the film plane (2-12).
In particular, for s-PS films, three different kinds of uniplanar orientations can be achieved by simple procedures involving co-crystallization in the presence of suitable guest molecules (solution crystallization (2-4)solvent-induced crystallization in amorphous samples (5-7) or solvent-induced recrystallizations of suitable crystalline films (8)). The three observed uniplanar orientations correspond to the three simplest orientations of a high planar-density layer (formed by close-packed alternated enantiomorphous s-PS helices) with respect to the film plane (9-10). As for PPO, two different kinds of uniplanar orientations have been obtained by co-crystallization, as induced by different guests in amorphous films (11).Recently it was found that suitable guest molecules that are able to co-crystallize with poly(L-lactic acid) (PLLA) canalso generate uniplanar orientations of co-crystalline phases, by low-temperature sorption inamorphous unoriented PLLA films (12).
As for PPO it is worth underlining that due to the absence of fiber spectra, the occurrence of uniplanar orientation may be particularly useful to solve the PPO co-crystal structure as well as the related nanoporous-crystalline modification.
In this communication we will present a new kind of crystalline phase orientation developed on PPO polymeric films by casting procedures.

References

1. 1 Alexander, L. E. In X-ray diffraction methods in Polymerscience; Robert E. Krieger: Huntington, NY, 1979; Chapter4, pp 210-211.;*36*, 8695-8703.
2. Rizzo, P.; Lamberti, M.; Albunia, A. R.; Ruiz de Ballesteros, O.; Guerra, G. *Macromolecules* 2002, *35*, 5854-5860.
3. Rizzo, P.; Costabile, A.; Guerra, G. *Macromolecules* 2004, *37*, 3071-3076.
4. Daniel, C.; Avallone, A.; Rizzo, P.; Guerra, G. *Macromolecules* 2006, *39*, 4820–4823.
5. Rizzo, P.; Albunia, A. R.; Milano, G.; Venditto, V.; Guerra, G.; Mensitieri, G.; Di Maio, L. *Macromol. Symp.* 2002, *185*, 65-75.
6. Rizzo, P.; Della Guardia, S.; Guerra, G. *Macromolecules* 2004, *37*, 8043-8049.
7. Rizzo, P.; Spatola, A.; De Girolamo Del Mauro, A.; Guerra, G. *Macromolecules* 2005, *38*,10089-10094.
8. Rizzo, P.; Albunia, A. R.; Guerra, G. *Polymer* 2005, *46*, 9549–9554.
9. Albunia, A. R.; Rizzo, P.; Guerra, G. *Chem. Mater.* 2009, *21*, 3370-3375.
10. Albunia, A. R.; Rizzo, P.; Tarallo, O.; Petraccone, V.; Guerra, G. *Macromolecules* 2008, *41*,8632-8642.
11. Guerra, G.; Daniel, C.; Rizzo, P.; Tarallo, O. *J. Polym. Sci. Polym. Phys. Ed.* 2012, *50*, 305-322
12. Rizzo, P.; Ianniello, G.; Longo, S.; Guerra, G. *Macromolecules* 2013, *46*, 3995-4001.

Sustainable biochemicals production by esterification reaction using heterogeneous catalysts

Riccardo Tesser[a],*Rosa Vitiello*[a], *Rosa Turco*[a], *Vincenzo Russo*[a], *Antonio Buonerba*[b], *Alfonso Grassi*[b], *Martino Di Serio*[a]

[a] *University of Naples Federico II, Naples, 80126, Italy;*
[b] *University of Salerno, Fisciano (Sa), 84084, Italy;*
e-mail: riccardo.tesser@unina.it

Waste raw materials obtained by several sources of both food and agro industries could be considered for biomaterials production. In the last years, this topic was growing in interest, in particular considering oleins, mixtures of free fatty acids (FFAs) and glycerides. The purpose of this study is related the investigation of the performances of synthetic acid resin (sPSB-SA) as a new heterogeneous catalyst characterized by a high stability at high temperatures (180°C). This catalytic system was tested in esterification reaction in order to obtain bio-chemicals (such as plasticizers or surfactants) and bio-lubricants (an alternative to the petrochemical lubricants).
Typical catalysts used for the esterification reaction are acid homogeneous catalysts such as p-toluen-sulfonic acid, phosphoric acid, sulfuric acid [1]. The use of classic heterogeneous catalysts such as acid resins is instead limited by the fact that they are not stable at temperatures higher than 120°C [2]. For the esterification of FFAs, for different applications such as bio-lubricants synthesis or bio-chemicals synthesis the temperature must be higher than 180°C to favor the elimination of water from the reaction environment because the reaction is limited by chemical equilibrium.
For these reasons the objective of this study has been the investigation of the performances of synthetic acid resin (sPSB-SA) as a heterogeneous catalyst characterized by a high stability at high temperatures (180°C) [3]. This catalytic system has been successfully tested in the above mentioned esterification reaction and compared to classic commercial strong acid catalysts like Amberlyst®, Nafion® and sulfuric acid. The catalytic system was tested in a batch reactor and a loop reactor, in order to verify the catalyst stability. The esterification reaction was performed using different polyalcohols with saturated monocarboxylic acids.
In particular, the reaction was performed using oleic acid, as references of fatty acid from biomasses, and 1,3-propanediol, pentaerythritol, trimethylolpropane as alcohols, in order to obtain different bio-lubricants bases. The second reactive system, instead, used oleic acid and glycerol in order to obtain bio-chemicals.The typical reaction conditions were chosen as follows: the temperature was 180°C, the molar ratio (considering the function groups) was 1:1, the catalyst was variable.
Acid resin (reticulated and not-reticulated) has shown high activity in esterification reaction and a good resistance to the deactivation. The specific activity of the sPSB-SA resins (referred to the acid equivalent) is similar than that of sulfuric acid in the conversions of FFA. The introduction of crosslinks in the resin reduces the overall acidity of the resin and, consequently, its activity but sPSB-SA2 is more stable and it can easily be separated from the reaction products. The results showed that the synthetic resins sPSB-SA1 and sPSB-SA2 (reticulated) had similar activity of sulfuric acid, in particular the resin showed higher activity than all catalysts tested.

References

1. J.A. Melero, J. Iglesias, G. Morale; Green Chem. 2009,11, 1285-1308.
2. M. Di Serio, R. Tesser, M. Dimiccoli, F. Cammarota; M. Nastasi, E. Santacesaria; J. Mol. Catal. A: Chem. 2005, 239, 111–115.
3. R. Vitiello; A. Buonerba; R. Tesser; M. Di Serio; A. Grassi; E. Santacesaria. DGMK-Tagungsbericht 2012, 3, 49-55.

Flagship demonstration of an integrated biorefinery for dry crops sustainable exploitation towards biobased materials production

Andrea Vassoi[a], *Massimiliano Mari* [a], *Stefania Solmi* [a], *Fabrizio Cavani* [a]

[a] *Dipartimento di Chimica Industriale "Toso Montanari", Università degli studi di Bologna*
Viale del Risorgimento, 4, 40136, Bologna, Italy;
e-mail: andrea.vassoi2@unibo.it

The role of University of Bologna team, a partner of the Flagship First2Run project, is focused on the study of the catalytic process for the transformation of fatty esters (triglycerides) and fatty acids into shorter dicarboxylic acids, more specifically the oxidative cleavage of oleic acid (or the corresponding triglyceride), from cardoon flower, into Pelargonic acid and Azelaic acid (or the corresponding ester). These acids are industrially used as component in a series of applications such as polyamides, polyesters, cosmetics, pharmaceuticals, plasticizers, lubricants, or hydraulic fluids (1). This process is currently carried out in industry with ozone as the oxidant, which however implies the use of dangerous process conditions. Matrìca, a joint venture between Versalis and Novamont, has developed a process for the oxidative cleavage in two-steps, consisting first in an hydroperoxidation of the triglyceride to the corresponding glycol and then in the oxidative cleavage of the glycol into the shorter chain acids (2) (Figure 1). Aim of my research work will be to investigate various options for the catalytic oxidation of fatty acids and esters, by means of more sustainable oxidants and catalysts. For example, one option will be the design and implementation of a heterogeneous catalyst for the oxidative cleavage step.

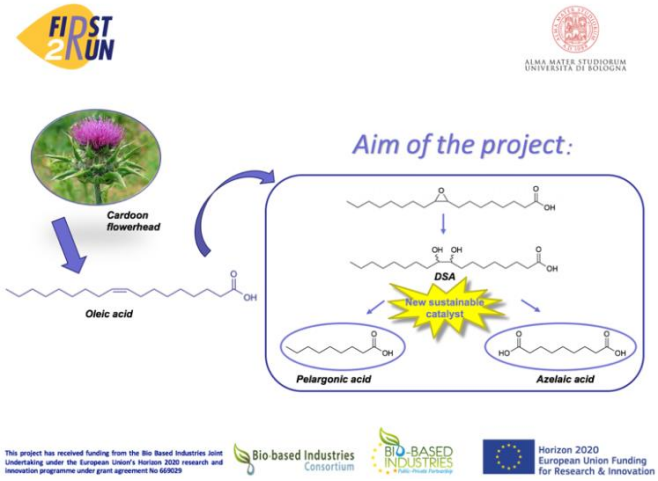


Figure 6: Main reaction pathways for the cleavage of oleic acid to Azelaic acid and Pelargonic acid.

Acknowledgements. This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 669029

References

1. *Ullmann's Encyclopedia of Industrial Chemistry*, Release, 7th Edition, Wiley-VCH, Weinheim 2010.
2. Bastioli C., Milizia T., Borsotti G., US Patent 0245995 (2008).

Elenco degli Autori

*Indica l'autore presentatore

	IND OR31
	IND OR33
	IND PO12
D'Ottavio Massimo	IND FC13
Duchon Tomas	IND PZ01
Dyballa Michael Martin	IND OR15
Evangelisti Claudio	IND OR03
	IND OR32
	IND PO05
Falco Marisa	IND OR17
Ferrari Giorgio*	IND OR27
Ferri Dino	IND OR24
Figoli Alberto	IND OR28
Fini Paola	IND PO08
Fonda Emiliano	IND PZ01
Fornasiero Paolo	IND PZ01
Frison Francesco	IND OR13
Frusteri Francesco	IND OR02
Fulignati Sara	IND OR30
Fusco Caterina	IND PO08
Fuso Nerini Ivan	IND OR06
Gabriele Bartolo	IND OR28
Galdi Nunzia	IND FC05
Galiano Francesco	IND OR28
Galliano Simone*	IND OR17
Galloni Pierluca	IND OR12
Gargani Elisabetta	IND OR23
Gerbaldi Claudio	IND OR14
	IND OR17
	IND FC01
Gerosa Matteo	IND PO01
Ghedini Elena*	IND OR22
Gignone Andrea	IND FC06
Giomi Donatella	IND FC13
	IND PO02
Giordano Fabrizio	IND OR17
Giurlani Walter	IND OR25
Gomez Bernal Hilda	IND FC08
Gorte Raymond J.	IND PZ01
Grassi Alfonso	IND OR21
	IND PO06
	IND PO12
Grätzel Michael	IND OR14
	IND OR17
Groppi Gianpiero	IND OR05
Grossi Bernardo	IND FC13
Guerra Gaetano	IND FC12
	IND PO10
Guidotti Matteo*	IND OR23
	IND PO05
Hagfeldt Anders	IND OR14
	IND OR17
Hoinkis Jan	IND OR28
Iaquaniello Gaetano*	IND IL01
Innocenti Giada*	IND FC04
Innocenti Massimo	IND FC02
Innocenti Massimo*	IND OR25
Iodice Mario	IND PO10
Khader Mahmoud M.	IND PZ01

Lamberti Carlo	IND OR15
Lamparelli David Hermann*	IND FC05
Lapenta Rosita*	IND OR21
	IND PO06
Laurenza Amelita Grazia	IND PO08
Lavallata Vito	IND OR08
Leone Federica*	IND FC06
Leonelli Cristina	IND OR19
Leonzio Grazia*	IND FC03
Licini Giulia	IND OR09
Licursi Domenico*	IND OR30
Livia Della Seta	IND OR06
Lomachenko Kirill A.	IND OR15
Longo Aldo	IND OR24
Lova Paola	IND PO10
Lucarelli Carlo	IND FC11
Luo Jing	IND PZ01
Malafronte Anna*	IND OR26
Malavolti Marino*	IND FC07
Mali Matilda	IND OR19
Malmusi Andrea	IND FC04
Mancino Donato	IND OR09
Mancuso Raffaella*	IND OR28
Manna Luigi	IND FC06
Manzoli Maela	IND FC14
Mari Massimiliano	IND PO13
Maria Carewska	IND OR06
Mariottini Stefano	IND OR25
Maroto-Valer Mercedes	IND FC14
Martini A.	IND OR15
Martino Di Serio*	IND PO04
Martinuzzi Stefano	IND OR25
	IND FC02
Mastrorilli Piero	IND OR19
Matolin Vladimir	IND PZ01
Mauriello Francesco	IND OR04
Mazzocca Marcella	IND OR33
Melloni Mattia*	IND FC08
Menegazzo Federica	IND PO09
Menegazzo Federica*	IND PO07
Meschisi Luca	IND FC13
Mezzapica Aldo	IND OR02
Milione Stefano	IND OR21
	IND PO06
Monai Matteo*	IND PZ01
Monari Magda	IND OR21
Montini Tiziano	IND PZ01
Muñoz-García Ana Belen	IND PZ02
Murray Christopher B.	IND PZ01
Nacci Angelo	IND PO08
Nair Jijeesh	IND FC01
Navarra Wanda	IND OR18
Navarra Wanda*	IND FC09
Negri Chiara	IND OR15
Negro Enrico	IND OR16
Niphadkar Prashant	IND PO05
Nodari Mirco*	IND OR24
Novelli Mario	IND PZ06
Oliva Leone	IND FC05

Olivo Alberto	IND FC14
Olsbye Unni	IND OR15
Onida Barbara	IND FC06
Pace Giuseppe	IND OR16
Pallavicini Marco	IND OR10
Pantone Vincenzo*	IND PO08
Paone Emilia*	IND OR04
Pappas Dimitrios	IND OR15
Passaponti Maurizio	IND OR25
Passarini Fabrizio	IND FC15
Patrini Maddalena	IND PO10
Pavarelli Giulia	IND FC11
Pavone Michele	IND PZ02
Pereira-Henrández Xavier Isidro	IND OR03
Perolo Andrea	IND OR24
Picchi Claudio	IND FC02
Piciollo Emanuele	IND OR25
	IND FC02
Pietropaolo Rosario	IND OR04
Pirola Carlo	IND OR01
Pirri Candido F.	IND PO01
Pizzolitto Cristina	IND PO07
Pizzolitto Cristina*	IND PZ03
	IND PO09
Praglia Veronica*	IND FC10
Prati Laura	IND OR01
	IND OR11
Prosini Pier Paolo*	IND OR06
Proto Antonio	IND FC15
Psaro Rinaldo	IND OR23
	IND OR32
	IND PO05
Puzzo Francesco*	IND FC11
Quaglio Marzia	IND PO01
Ramis Gianguido	IND OR01
	IND FC10
Rappuoli Roberto	IND OR23
Raspolli Galletti Anna Maria	IND OR30
	IND FC08
Rastrelli Federico	IND OR29
Ravasio Nicoletta	IND OR32
	IND PO05
Riccardo Tesser	IND PO04
Ricciardi Maria*	IND FC15
Rizzo Paola	IND FC12
Rizzo Paola*	IND PO10
	IND PO11
Rizzuti Antonino	IND OR19
Rodolfi Liliana	IND FC13
Romanazzi Giuseppe	IND OR19
Ronchetti Silvia	IND FC06
Rosa Turco	IND PO04
Rosa Vitiello	IND PO04
Rosi Luca	IND OR25
Rossetti Ilenia	IND OR01
	IND OR11
	IND FC10
	IND FC14
Russo Antonella	IND PO08

Russo Vincenzo	IND OR20
	IND OR33
	IND PO12
Russo Vincenzo*	IND OR31
Sabuzi Federica*	IND OR12
Sacco Adriano	IND PO01
Sacco Olga	IND FC09
Sacco Olga*	IND OR18
Salvietti Emanuele	IND OR25
	IND FC02
Salvini Antonella	IND PO02
Salvini Antonella*	IND FC13
Sasso Carmen	IND OR26
Savara Aditya	IND OR11
Scalia Alberto	IND PO01
Schiraldi Chiara	IND OR33
Schiro' Antonietta	IND FC07
Scotti Nicola*	IND OR32
Semenzato Alessandra	IND OR22
Signoretto Michela	IND OR22
	IND PO07
	IND PO09
Signoretto Michela*	IND FC14
Solmi Stefania	IND PO13
Svelle Stian	IND OR15
Tabanelli Tommaso*	IND PZ05
Tesser Riccardo	IND OR20
	IND OR31
	IND OR33
Tesser Riccardo*	IND PO12
Tredici Mario	IND FC13
Tresso Elena	IND PO01
Trifirò Ferruccio	IND OR34
Tripodi Antonio	IND OR01
Tronconi Enrico	IND OR05
Turco Rosa	IND OR20
	IND OR31
	IND PO12
Turco Rosa*	IND OR33
Vaiano Vincenzo	IND OR18
	IND FC09
Vassoi Andrea*	IND PO13
Vassura Ivano	IND FC15
Venditto Vincenzo	IND OR18
	IND FC09
Vezzù Keti	IND OR16
Villa Alberto*	IND OR11
Villani Vincenzo*	IND OR08
Vincenzo Russo	IND PO04
Viscardi Guido	IND OR17
Vitale Vissia	IND PO11
Vitiello Rosa	IND OR31
	IND OR33
	IND PO12
Vitiello Rosa*	IND OR20
Wang Yong	IND OR03
Zaccheria Federica	IND OR32
Zanardo Danny	IND PO09
Zecca Marco	IND OR29

Zecca Marco*	IND OR13
Zonta Cristiano	IND OR09

DIVISIONE DI CHIMICA INORGANICA

Comitato Scientifico

- Adriana Saccone, Università di Genova
- Roberto Gobetto, Università di Torino
- Alberto Credi, Università di Bologna
- Emma Gallo, Università di Milano
- Gaetano Granozzi, Università di Padova
- Alceo Macchioni, Università di Perugia
- Michele Saviano, Consiglio Nazionale delle Ricerche, Bari
- Francesco Paolo Fanizzi, Università del Salento
- Paolo Fornasiero, Università di Trieste

Delegato di Divisione

- Chiara Costabile, Università degli Studi di Salerno

Programma scientifico

Divisione di Chimica Inorganica

Lunedì 11 Settembre 2017

	Sala Nettuno
	Sessione I
	Chairperson Francesco Paolo Fanizzi
9:00 – 9:45	INO-PL01: J. A. van Bokhoven *Action at a distance: observing hydrogen spillover*
9:45 – 10:15	INO-KN01: M. Chiesa *Exploring and Engineering Spin-states in Solid State and Surface Chemistry*
10:15 – 10:30	INO-OR01: T. Kosmala, L. Calvillo, S. Agnoli, G. Granozzi *New methods and new catalysts for the oxygen reduction reaction at the cathode of fuel cells: surface science applied to CoO_x/Pd(100) ultrathin films.*
	Sala Mercurio
	Sessione II
	Chairperson Luigi Monsù Scolaro
9:45 – 10:15	INO-KN02: M. Ravera *Dual-targeting hybrid anticancer platinum(IV) prodrugs for combination therapy.*
10:15 – 10:30	INO-OR02: D'Alonso, Linda Leone, Marco Chino, Ornella Maglio, Flavia Nastri, Vincenzo Pavone and Angela Lombardi. *Control of enzymatic activity in a Mn-containing synthetic metalloenzyme.*
10:30 – 11:00	Coffee Break
	Sala Nettuno
	Sessione I
	Chairperson Alberto Albinati
11:00 – 11:30	INO-KN03: R. Zanoni *Highly delocalized stable systems on semiconductor surfaces*
11:30 – 11:45	INO-OR03: D. Cherni, N. Moussa, M. F. Ncib, L. Prati, A. Villa *Effect of N-doping in the activity of TiO_2 supported catalysts in glycerol oxidation*
11:45 – 12:00	INO-OR04: P. Solokha, S. De Negri, A. Saccone *Long Period Stacking Ordered phases in the Y-Ni-Mg system: experimental and structural studies*
12:00 – 12:15	INO-OR05: M. Benedetti, F. De Castro[a], F. P. Fanizzi *General cooperative effects of single atom ligands on the ^{73}Ge, ^{119}Sn and ^{207}Pb NMR signals of tetrahedral [MX_4] (M = Ge, Sn, Pb; X_4 = combination of Cl, Br, I) coordination compounds*
12:15 – 12:30	INO-OR06: F. Barzagli, C. Giorgi, F. Mani, M. Peruzzini *CO_2 capture by aqueous Na_2CO_3 combined with the formation of high quality $CaCO_3$ and the release of pure CO_2 at room conditions*
12:30 – 12:45	INO-OR07: M. La Rosa , S. Silvi, G. Jonusauskas, N. D. McClenaghan, A. Credi *Long-lived luminescent Quantum Dots as result of Reversible Electronic Energy Transfer*
12:45 – 13:00	INO-OR08: G. V. Bianco, M. Grande, L. La Notte, E. Villari, M. M. Giangregorio, M. Losurdo, P. Capezzuto, A. Reale, A. D'Orazio, G. Bruno *Grafene Functionalization and Tuning of Transport Properties by Plasma Strategies*
	Sala Mercurio
	Sessione II
	Chairperson Nazzareno Re
11:00 – 11:30	INO-KN04: L. Monsù Scolaro *On the chirality in porphyrin nanoassemblies.*

11:30 – 11:45	INO-OR09: I. Venditti, M. Porchia, F. Tisato, C. Santini, M. Pellei, G. Iucci, C. Battocchio, C. Pietrosanti, G. Testa , I. Fratoddi *Drug delivery systems: hydrophilic gold nanoparticles for controlled drug loading and release.*
11:45 – 12:00	INO-OR10: L. Conti, A. Bencini, M. G. Fabbrini, C. Gellini, C. Giorgi, G. Pietraperzia, B. Valtancoli *Novel strained ruthenium complexes in photodynamic therapy*
12:00 – 12:15	INO-OR11: S. Concilio, L. Sessa, A. Massa, S. Piotto, P. Iannelli, R. Diana, B. Panunzi, U. Caruso *Fluorescent solvatochromic molecules as probes for lipid bilayers*
12:15 – 12:30	INO-OR12: S. Samaritani, D. Belli Dell' Amico, M. Colalillo, L. Labella, F. Marchetti, M. Hyeraci, A. N.García-Argáez, L. Dalla Via *Platinum(II) complexes of ligands containing OH functional groups: synthesis, reactivity and antiproliferative properties*
12:30 – 12:45	INO-OR13: L. Izzo, M. De Rosa, G. Vigliotta, A. Soriente, V. Capaccio, G. Gorrasi, R. Adami, E. Reverchon, M. Mella *Killing bacteria via ion-complexing polymeric materials*
12:45 – 13:00	INO-OR14: D. Cirri, T. Marzo, A. Pratesi, L. Messori *Novel gold(I) and silver(I) metal complexes as promising antibacterial candidates*
	Sala Argiva
Sessione Congiunta Chimica Organica - Chimica Inorganica (GICO)	
Chairperson Antonella Dalla Cort	
11:30 – 12:00	ORG/INO KN01: Alessandro Caselli *Catalytic Applications of Pyridine-Containing Macrocyclic Complexes*
12:00 – 12:30	ORG/INO-PZ01: **EurJOC** Junior Organometallic Chemist Lecture by Valentina Pirovano *Gold(I)-catalyzed [4+2] cycloaddition reactions of vinylindoles and allenes*
12:30 – 12:45	ORG/INO-OR01: Elia Matteucci, Andrea Baschieri, Cristiana Cesari, Rita Mazzoni, Claudia Bizzarri, Letizia Sambri *Functionalized triazolylidenes as versatile mesoionic carbenes: metal complexes for catalysis and luminescent materials*
12:45 – 13:00	ORG/INO-OR02: Andrea Squarcina, Martina Zonzin, Mauro Carraro, Marcella Bonchio *Copper complexes with biomimetic antioxidant activity*

13:00 – 14:00	Intervallo Pranzo - – Lunch Break

	Sala Paestum B
14:00-15:00	*Sessione Poster 1 (INO PO01 – INO PO10)*
	Sala Nettuno
Sessione I	
Chairperson Michele Saviano	
15:00 – 15:45	INO-PL02: P. Carloni *Multiscale simulation-based structural predictions of metalloproteins of pharmacological relevance*
15:45 – 16:15	INO-KN05: L. Zaccaro, A. Del Gatto, L. Russo, B. Farina, A. Liguoro, S. Di Gaetano, D. Capasso, D. Comegna, R. Fattorusso, M. Saviano *RGDechi chimeric peptide as new scaffold for gaining insight into structural features of integrins selectivity for theranostics*
16:15 – 16:30	INO-OR15: D. La Mendola, G. Pandini, C. Satriano, A. Pietropaolo, I. Naletova, F. Gianì, A. Travalia, V. G. Nicoletti, G. Arena, E. Rizzarelli *The inorganic side of neurotrophins: metal coordination and new therapeutic perspectives*

	Sala Mercurio
	Sessione II
	Chairperson Alceo Macchioni
15:45 – 16:15	INO-KN06: F. Ragaini *Schiff Bases of the BIAN Family: from Symmetrical Biaryl Derivatives to Mixed, Alkyl, Chiral or Reduced Ligands and Heterogeneous Catalysts*
16:15 – 16:30	INO-OR16: R. Gobetto, C. Nervi *Homogenous and Heterogeneous Transition Metal Catalysts for CO_2 Reduction*
16:30 – 17:00	Coffee Break
	Sala Nettuno
	Sessione I
	Chairperson Chiara Gabbiani
17:00 – 17:15	INO-OR17: A. Mariconda, P. Longo, C. Saturnino, R. Lemba, M. S. Sinicropi *A new series of Ag and Au carbene complexes with interesting anticancer properties*
17:15 – 17:30	INO-OR18: M. I. Nardella, V. Mangini, A. Rosato, F. Arnesano, G. Natile *NMR studies on copper transport proteins interacting with silver nanoparticles*
17:30 – 17:45	INO-OR19: M. P. Donzello, E. Viola, C. Ercolani *New Differently Sized Neutral and OctacationicPorphyrazines. Physicochemical Properties and Potentialities as Anticancer Drugs*
17:45 – 18:00	INO-OR20: T. Marzo, D. Cirri, C. Gabbiani, A. Pratesi, T. Gamberi, F. Magherini, A. Guerri, T. Biver, A. Arcangeli, L. Messori *Auranofin, Et_3PAuCl and Et_3PAuI exert high in vitro cytotoxic effects toward colorectal cancer cell lines: a comparative chemical, biological and mechanistic study*
18:00 – 18:15	INO-OR21: V. Firpo, G. Zambrano, V. Pavone, K. L. Bren, A.Lombardi *Hydrogen Evolution Catalyzed by Cobalt Mimochrome VIa*
18:15 – 18:30	INO-OR22: E. Gabano, S. Gama, R. Vilar, M. Ravera, D. Osella *Bifunctional triamine Pt(II) complexes containing a DNA intercalating moiety*
18:30 – 18:45	INO-OR23: L. Leone, M. Chino, O. Maglio, V. Pavone, F. Nastri, A. Lombardi *Minimizing the release of reactive intermediates in O_2-dependent oxidation byde novo metalloenzymes*
	Sala Mercurio
	Sessione II
	Chairperson Roberto Gobetto
17:00 – 17:15	INO-OR24: C. Capacchione, M. Naddeo, E. Luciano, A. Buonerba, A. Grassi, A. Proto *Biosourced Polymers from Stereoregular Polymerization of Monoterpenes in the Presence of Homogeneous Titanium Catalysts.*
17:15 – 17:30	INO-OR25: D. Intrieri, D. M. Carminati , E. Gallo *Sustainable synthesis of aziridines: versatile precursors of fine chemicals*
17:30 – 17:45	INO-OR26: G. Manca, A. Ienco, M. Peruzzini, C. Mealli *Aspects of the Functionalization of the Phosphorene Surface*
17:45 – 18:00	INO-OR27: M. Mazzeo, F. Isnard, M. Lamberti, C. Pellecchia *Polyesters from the Alternating Copolymerization of Epoxides and Cyclic Anhydrides*
18:00 – 18:15	INO-OR28: L. Fagiolari , G. Patzke , A. Macchioni *Water Oxidation catalyzed by Ir(III) and Ru(III)-doped hydrotalcite-like compounds*
18:15 – 18:30	INO-OR29: R. Diana, F. Borbone, U. Caruso, S. Concilio, S. Piotto, B. Panunzi, A. Tuzi *New Self-Assembling Luminescent Materials from Pyridyl Oxadiazole Zn(II) Complexes*
18:30 – 18:45	INO-OR30: C. Garino, G. Volpi, C. Barolo, R. Gobetto, C. Nervi, M. D. Weber, R. D. Costa *Luminescent complexes and their bright ligands*
	Sala Nettuno
18:45 – 20:00	*Assemblea dei Soci della Divisione di Chimica Inorganica*

Martedì 12 Settembre 2017

	Sala Nettuno
	Sessione I
	Chairperson Maurizio Peruzzini
9:00 – 9:45	INO-MD01: G. Bertrand *Stable carbenes and related species as powerful tools in inorganic chemistry* ***Medaglia Sacconi***
9:45 – 10:15	INO-PZ01: G. Ragazzon, S. Silvi, A. Credi *Operating Molecular Machines: Thermodynamic and Kinetic Aspects* ***Premio miglior tesi di Dottorato***
10:15 – 10:30	INO-IL01: A. J. T. Shore *Publishing your research in high impact journals*
	Sala Puccini (Hotel Savoy)
	Sessione Congiunta Chimica Teorica - Chimica Inorganica
	Chairperson Gianluca Ciancaleoni
9:00 – 9:40	TEO/INO-KN01: B. Civalleri *Ab initio modeling of Metal-Organic Frameworks: from gas adsorption to stimuli responsive properties*
9:40 – 10:00	TEO/INO-OR01: A.B. Muñoz-García, M. Pavone *Computational design of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO)-based bifunctional electrodes for proton-conducting solid oxide electrochemical cells*
10:00 – 10:20	TEO/INO-OR02: M. Cutini, M. Corno, P. Ugliengo *Insight From DFT Simulations On The Collagen/Hydroxyapatite Interface: A Simple Model Based On The Poly-Proline Polymer*
10:20 – 10:40	TEO/INO-OR03: L. Falivene, S. Kozlov, L. Cavallo *A DFT Rationalization of a Two Metals Strategy to Tune Selectivity in Catalysis*
10:30 – 11:00	Coffee Break
	Sala Nettuno
	Sessione I
	Chairperson Gaetano Granozzi
11:00 – 11:30	INO-KN07: D. Armentano, E. Pardo, A. Leyva–Pérez, A. Corma *Synthesis and X-ray Snapshots of Ultrasmal Metallic Clusters within Metal-Organic Frameworks for High Performance in Catalysis.*
11:30 – 11:45	INO-OR31: M. Perfetti, M. Serri, L Poggini, M Mannini, D Rovai, P Sainctavit, S Heutz, R Sessoli *Layer by layer order of molecular thin films detected by Torque Magnetometry*
11:45 – 12:00	INO-OR32: *F. Tessore, G. Di Carlo, A. Orbelli Biroli, M. Pizzotti* Porphyrin-Sensitized Solar Cells: the challenge of photostability
12:00 – 12:15	INO-OR33: M. Melchionna, F. Paolucci, M. Bonchio, F. Vizza, P. Fornasiero, M. Prato *Hierarchical materials based on carbon nanostructures as advanced catalysts in energy applications*
12:15 – 12:30	INO-OR34: A. Carella , R. Centore, M. Bonomo, D. Dini, A. Di Carlo *Pyran based dyes as photosensitizers for p-type dye-sensitized solar cells*
12:30 – 12:45	INO-OR35: A. G. Marrani, D. Giacco, R. Zanoni, S. Brutti *Unravelling the surface degradation mechanisms in ether electrolyte based Li-O_2 cells*
12:45 – 13:00	INO-OR36: I. Fratoddi, I. Venditti, L. Fontana, C. Sibilia, G. Leahu, A. Belardini, R. Li Voti, C. Battocchio, R. Matassa, G. Familiari *Networks based on functionalized noble metal nanoparticles: advanced materials for optical and electronic applications*

	Sala Mercurio
Sessione II	
Chairperson Emma Gallo	
11:00 – 11:30	INO-KN08: C. Tubaro, M. Baron *Selective syntheses of mononuclear vs dinuclear gold(III) complexes with di(N-heterocyclic carbene) ligands*
11:30 – 11:45	INO-OR37: C. Femoni, G. Bussoli, I. Ciabatti, M. Ermini, M.Hayatifar, M. C. Iapalucci, S. Ruggieri, S. Zacchini *New examples of interstitial Bismuth atoms in icosahedral rhodium cages*
11:45 – 12:00	INO-OR38: M. Atzori, L. Tesi, E. Morra, M. Chiesa, L. Sorace, R. Sessoli *Synthetic Strategies Towards Quantum Coherence Time Enhancement in Potential Molecular Spin Qubits*
12:00 – 12:15	INO-OR39: F. Grisi, V. Paradiso, C. Costabile, V. Bertolasi *Olefin Metathesis Ruthenium Catalysts Bearing Backbone-Substituted Unsymmetrical NHC Ligands*
12:15 – 12:30	INO-OR40: L. Armelao, D. Belli Dell'Amico, G. Bottaro, L. Labella, F. Marchetti, S. Samaritani *4,4' bipyridine monoxide (bipyMO): a simple heterotopic divergent ligand*
12:30 – 12:45	INO-OR41: L. Luconi, G. Tuci, A. Rossin, G. Giambastiani *Catalysis by Group IV Amido-Pyridinate Complexes for the Reduction of Carbon Dioxide to Methane*
12:45 – 13:00	INO-OR42: M. Monticelli, M. Baron, A. Longhi, C. Tubaro, S. Bellemin-Laponnaz, C. Graiff, M. Rancan, G. Bottaro, L. Armelao *Dinuclear d^{10} complexes with nNHC/tzNHC heteroditopic carbene ligands and their luminescence properties*
	Sala Puccini (Hotel Savoy)
Sessione Congiunta Chimica Teorica - Chimica Inorganica	
Chairperson Emilia Sicilia	
11:20 – 12:00	TEO/INO-KN02: I. Tolbatov, C. Coletti, A. Marrone, N. Re *Insight into the Electrochemical Reduction Mechanism of Pt(IV) Anticancer Complexes*
12:00 – 12:20	TEO/INO-OR04: T. Marino, M. Prejanò, P. Piazzetta, N. Russo *The role of metal substitution in the metallo-enzymes: A theoretical point of view*
12:20 – 12:40	TEO/INO-OR05: G. Ciancaleoni, N. Bartalucci, L. Belpassi, F. Marchetti *Back-donation in d^0 Metal Complexes: Does it Exist? The case of Nb(V)*
12:40 – 13:00	TEO/INO-OR06: G. Mazzone, C. Regina, N. Russo *Combination of Porphyrin and Ruthenium-arene moieties for a Dual Anticancer Function. A Theoretical Investigation*

13:00 – 14:00	Intervallo Pranzo

	Sala Paestum B
14:00-15:00	*Sessione Poster 2 (INO PO11 – INO PO24)*

Mercoledì 13 Settembre 2017

	Sala Paestum B
14:00-15:00	*Sessione Poster 3 (INO PO25 – INO PO38)*
	Sala Nettuno
Sessione Congiunta	
Chairperson Adriana Saccone	

15:00 – 15:45	INO-PZ02: M. Mannini *Exploring magnetism of molecules at the nanoscale* *Premio Nasini*
15:45 – 16:30	INO-PZ03: C. Landis *Organotransition Metal Complexes, Catalysis, and Industry* ***Premio Chini***
16:30 – 17:00	Coffee Break
	Sala Nettuno
	Sessione Congiunta Chimica Organica - Chimica Inorganica (GICO)
	Chairperson Fabio Ragaini
17:00 – 17:30	ORG/INO-KN02: L. Zani *Conjugated Organic Compounds for Solar Energy Conversion to Electricity and Fuels*
17:30 – 18:00	ORG/INO-PZ02: **EurJIC** Junior Organometallic Chemist Lecture by M. Bellini *Hydrogen and chemicals from renewable alcohols by Organometallic Electro-Reforming (OMER)*
18:00 – 18:15	ORG/INO-OR03: W. Baratta, R. Figliolia, S. Baldino, H. Günter Nedden, A. Zanotti-Gerosa *Mild N-Alkylation of Amines with Alcohols Catalyzed by Acetate Ruthenium Complexes*
18:15 – 18:30	ORG/INO-OR04: R. Mazzoni, C. Cesari, A. Cingolani, V. Zanotti, F. Cavani, F. Puzzo, C. Lucarelli, M. Mella, A. Tagliabue, T. Baker *The power of ligand combination in redox active ruthenium and iron complexes*
18:30 – 18:45	ORG/INO-OR05: R. Figliolia, S. Baldino, W. Baratta, S. Gibolout, H. Günter Nedden, A. Zanotti-Gerosa *Synthesis of New Carbonyl Diphosphane Ruthenium Complexes for Catalytic C-H Bond Activation Reactions*
	Sala Mercurio
	Sessione II
	Chairperson Alberto Credi
17:00 – 17:15	INO-OR43: E. Diana, E. Priola, F. Grifasi, R. Gobetto, M. R. Chierotti *Symbiotic structural and spectroscopic approach to reticular chemistry: the case study of luminescent Copper(I) cyanide coordination polymers.*
17:15 – 17:30	INO-OR44: S. Pragliola, A. Botta , V. Venditto, A. Velardo, R. Liguori , Alfredo Rubino *Polymer Stereoregularity Influence on Optical Properties of Carbazole-based Photoconductor Polymers*
17:30 – 17:45	INO-OR45: C. Daniel, P. Cortelletti, M. Pedroni, G. Antonio D'Amora, G. Guerra, A. Speghini *Upconverting polymeric aerogels*
17:45 – 18:00	INO-OR46: C. Crestini, H. Lang, e L. Zongo *Coordination Complexes and One Step Assembly of Natural Polyphenols for Versatile Nanocapsule Engineering*
18:00 – 18:15	INO-OR47: V. Nicolini, G. Malavasi, L. Menabue, G. Lusvardi, F. Benedetti, S. Valeri, P. Luches *Mesoporous bioactive glasses doped with cerium: investigation of catalase and SOD mimetic activities, and bioactivity*
18:15 – 18:30	INO-OR48: M. Marchini, A. Luisa, G. Bergamini, N. Demitri, M. Baroncini, P. Ceroni, E. Iengo *Tetrahedral Arrays of Metallo-porphyrins*
18:30 – 18:45	INO-OR49: M. La Deda, L. Sancey, G. Palermo, R. Termine, A. De Luca, E. I. Szerb, I. Aiello, A. Candreva, L. Ricciardi, M. Ghedini *Plasmonics Applied to a Nanotheranostic System: Synthesis, Photophysical Properties and Anticancer Activity of Silica/Gold Nanoparticles*

Medaglie e Premi della Divisione di Chimica Inorganica

***Medaglia Sacconi*:** Prof. Guy Bertrand, University of California San Diego

***Premio miglior Tesi di Dottorato*:** Dr. Giulio Ragazzon, Università di Bologna

***Premio Nasini*:** Prof. Matteo Mannini, Università di Firenze

***Premio Chini*:** Prof. Clark R. Landis, University of Wisconsin-Madison

***Premio under 35 EJOC*:** Dr.Valentina Pirovano, Università di Bologna

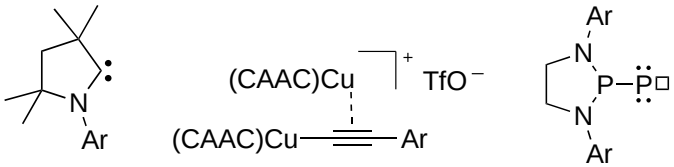
***Premio under 35 EJIC*:** Dr. Marco Bellini, Consiglio Nazionale delle Ricerche

Stable carbenes and related species as powerful tools in inorganic chemistry

Guy BERTRAND

UCSD-CNRS Joint Research Chemistry Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093-0358 (USA)
E-mail: guybertrand@ucsd.edu

It will be shown that the peculiar electronic and steric properties of cyclic (alkyl)(amino)carbenes (CAACs) **1** (1,2) and other stable singlet carbenes allow for the stabilization of unusual diamagnetic and paramagnetic main group element species. As examples, we will describe the preparation of room temperature stable boron, antimony-, and even carbon-centered neutral and cationic radicals.
We will also show that CAACs allow for the isolation of catalytically active complexes, which were supposed to be only transient intermediates. Among them, bis(copper) complexes **2** involved in the very popular CuAAC reaction (Click Chemistry) will be discussed (3)· We will show that this discovery allows for the development of novel catalytic transformations (4).
Another part of the lecture will be devoted to the synthesis, reactivity and coordination behavior of the first stable phosphinidene **3** (5,6,7).



1 **2** **3**

References:
1. M. Soleilhavoup, G. Bertrand, **Acc. Chem. Res. 2015**, *48*, 256-266.
2. M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, **Angew. Chem. Int. Ed. 2017**, *56*, DOI: 10.1002/anie.201702148
3. L. Jin, D. R. Tolentino, M. Melaimi, G. Bertrand, **Sci. Adv. 2015,** *1*, e1500304.
4. E. A. Romero, J. L. Peltier, R. Jazzar, G. Bertrand, **Chem. Sci. 2017**, *8*, 165-168.
5. L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, **Chem 2016**, *1*, 27-29.
6. M. M. Hansmann,, R. Jazzar, G. Bertrand, **J. Am. Chem. Soc. 2016**, *138*, 8356-8359.
7. M. M. Hansmann, G. Bertrand, **J. Am. Chem. Soc. 2016**, *138*, 15885-15888.

Operating Molecular Machines: Thermodynamic and Kinetic Aspects

Giulio Ragazzon[a,b], *Serena Silvi*[a], *Alberto Credi*[c,d]

[a] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna;* [b] *Present address: Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova;* [c] *Dipartimento di Scienze e Tecnologie Agro-alimentari, Università di Bologna, viale Fanin 50, 40127 Bologna;* [d] *Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, via Gobetti 101, 40127 Bologna.*

The Nobel Prize in Chemistry 2016 has been awarded "for the design and synthesis of molecular machines". Despite the incredible progresses of the field, several challenges still require substantial development. These include encoding functionality in simple structures, performing molecular tasks, implementing ratcheting mechanism and developing autonomous systems. In this talk, work aimed at tackling these challenges will be presented. In particular, spectroscopic and electrochemical techniques have been applied to the study of calixarene-based interlocked structures(1,2,3), functional rotaxanes(4,5,6) and pseudorotaxanes(7,8). The most relevant achievement has been the direct observation of a light-driven self-assembling molecular pump operating under nonequilibrium conditions(8).

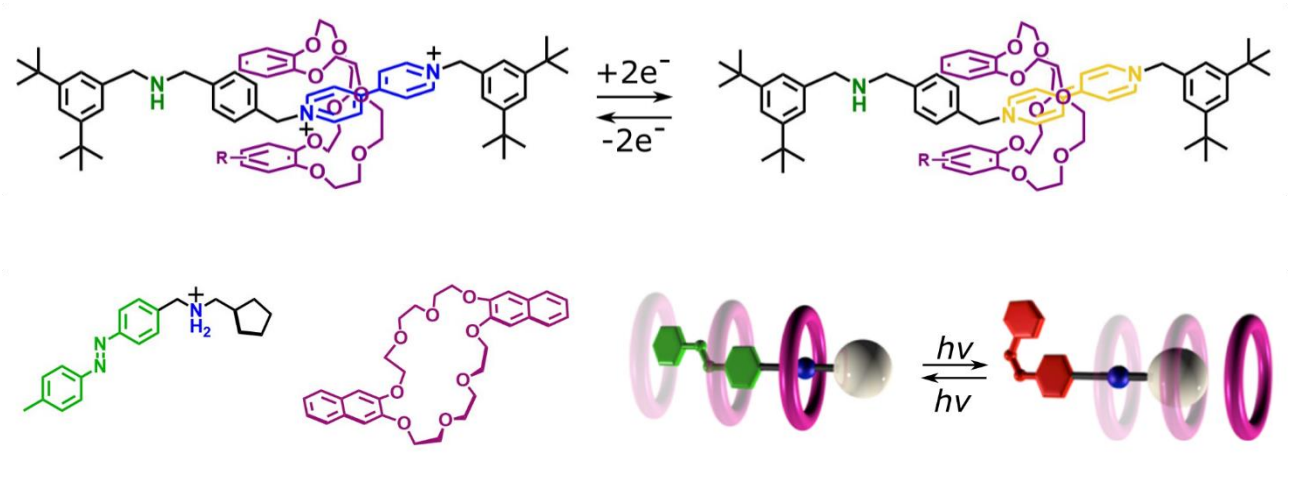


Figure 1: A rotaxane in which reduction of the secondary station affords a change in pKa at the primary station, due to the ability of the ring to put the two stations in communication (top); molecular components and minimal operation scheme of a light-driven self-assembling pump module (bottom).

References: 1. G. Orlandini, V. Zanichelli, A. Secchi, A. Arduini, G. Ragazzon, A. Credi, M. Venturi, S. Silvi, *Supramol. Chem.*, **2016**, 28, 427 - 435. 2. V. Zanichelli, G. Ragazzon, A. Arduini, A. Credi, P. Franchi, G. Orlandini, M. Venturi, M. Lucarini, A. Secchi, S. Silvi, *Eur. J. Org. Chem.*, **2016**, 1033 - 1042. 3. G. Orlandini, G. Ragazzon, V. Zanichelli, A. Secchi, S. Silvi, M. Venturi, A. Arduini, A. Credi, *Chem. Commun.*, **2017**, 53, 6172. 4. C. Schäfer, G. Ragazzon, B. Colasson, M. La Rosa, S. Silvi, A. Credi, *ChemistryOpen*, **2016**, 5, 2, 120 - 124. 5. P. Franchi, V. Bleve, E. Mezzanina, C. Schäfer, G. Ragazzon, M. Albertini, D. Carbonera, A. Credi, M. Di Valentin, M. Lucarini, *Chem. Eur. J.*, **2016**, 22, 8745 - 8750. Inside back cover. 6. G. Ragazzon, A. Credi, B. Colasson, *Chem. Eur. J.*, **2017**, 23, 2149 - 2156. 7. G. Orlandini, G. Ragazzon, V. Zanichelli, L. Degli Esposti, M. Baroncini, S. Silvi, M. Venturi, A. Credi, A. Secchi, A. Arduini, *ChemistryOpen*, **2017**, 6, 1, 64 - 72. 8. G. Ragazzon, M. Baroncini, S. Silvi, A. Credi, *Nat. Nanotechnol.*, **2015**, 10, 70 - 75. Personally designed journal cover. Highlights: E. Sevick, *Nat. Nanotechnol.*, **2015**, 10, 18 - 19; O. Graydon, *Nat. Photon.*, **2015**, 9, 13.

Exploring magnetism of molecules at the nanoscale

Matteo Mannini

Laboratory for Molecular Magnetism, Department of Chemistry "Ugo Schiff" &
INSTM Research Unit of Firenze, University of Firenze, Sesto Fiorentino (FI), Italy.
matteo.mannini@unifi.it

With their rich and chemically-tuneable properties, molecular materials stand out as a possible solution to the quest for innovative technologies. In particular, magnetic molecules represent a rich playground for chemists and physicists toward the development of novel molecule-based devices, whose functionality can be finely tuned through the rational design and bottom-up assembly of their molecular constituents. This idea explains the huge efforts of *molecular magnetism* (1) community for exploring the incorporation of magnetic molecules in devices for information and computation technologies, including spintronics and quantum computation.

To achieve this goal it was essential to combine the richness of coordination chemistry with nanostructuration protocols. In particular, the fragility of coordination bonds in metal-based magnetic cores required a careful selection/modification of molecules as well as an attentive tailoring of self-assembly and processing methods. A multi-technique characterization approach (2,3) was also adopted to monitor each step of the nanostructuration process and to evaluate the structural and magnetic integrity of molecules in the environment of a single-molecule-device.

Going beyond a morphological characterization, as provided by scanning probe methods, demands for surface sensitive techniques capable of probing the chemical and electronic properties of surface-supported molecules. A key role is played by investigation tools based on large-scale facilities, which allow to directly access the static and dynamic magnetic properties down to the nanoscale.

Here we will overview our most recent results achieved in the characterization of hybrid nanostructures obtained by assembling magnetic molecules on surfaces. We will follow the path that allowed to demonstrate that three important classes of magnetic molecules retain their peculiar behaviour at the nanoscale. These encompass ***single molecule magnets***, in which classical and quantum magnetic properties may coexist (4,5), ***spin crossover complexes*** and ***redox isomers***, which both feature two magnetically inequivalent states accessible by application of an external stimulus (6,7). Such promising results now pave the way for the next ongoing step, namely the realization of innovative multifunctional devices (8).

References:

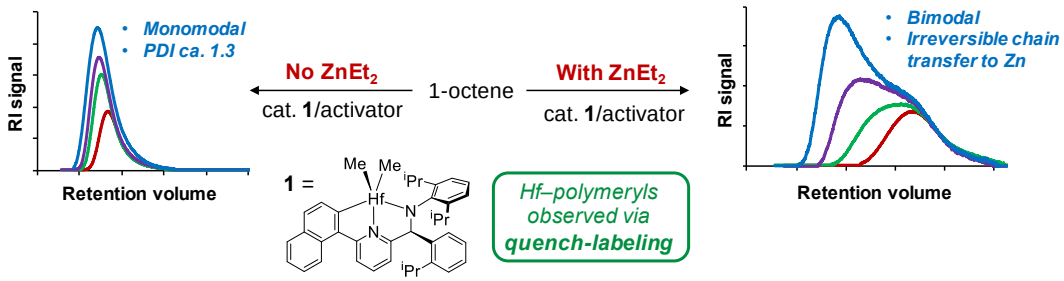
1. Gatteschi D, Sessoli R, Villain J. 2006. *Molecular Nanomagnets*. Oxford University Press
2. Cornia A, Mannini M. 2015. In *Structure and Bonding*, ed S Gao, pp. 293–330. Springer Berlin Heidelberg
3. Cornia A, Mannini M, Sainctavit P, Sessoli R. 2011. *Chem. Soc. Rev.* 40(6):3076–91
4. Mannini M, Bertani F, Tudisco C, Malavolti L, Poggini L, et al. 2014. *Nat. Commun.* 5:4582
5. Mannini M, Pineider F, Danieli C, Totti F, Sorace L, et al. 2010. *Nature*. 468(7322):417–21
6. Warner B, Oberg JC, Gill TG, El Hallak F, Hirjibehedin CF, et al. 2013. *J. Phys. Chem. Lett.* 4(9):1546–52
7. Poneti G, Poggini L, Mannini M, Cortigiani B, Sorace L, et al. 2015. *Chem. Sci.* 6(4):2268–74
8. Poggini L, Cucinotta G, Pradipto A-M, Scarrozza M, Barone P, et al. 2016. *Adv. Mater. Interfaces*. 3(14):1500855

Organotransition Metal Complexes, Catalysis, and Industry

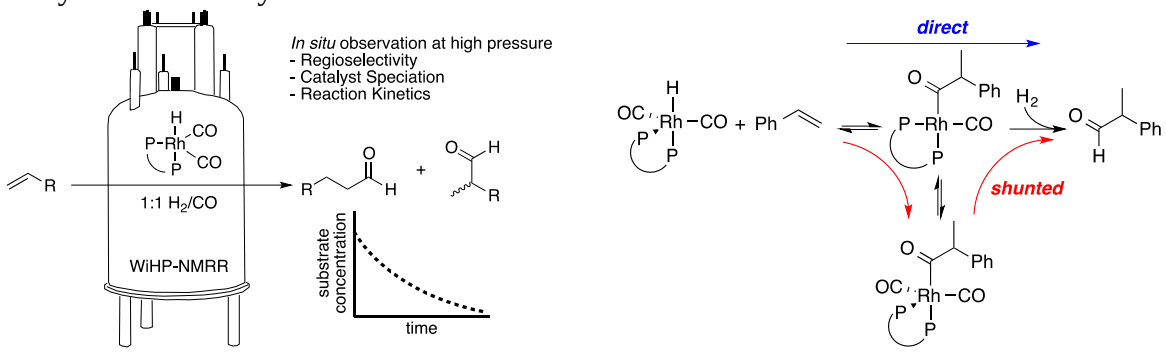
Clark R. Landis[a]

[a] *Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53705 USA; landis@chem.wisc.edu*

The rapid growth of organotransition metal chemistry in the last mid-century is tightly coupled with the implementation of organometallics in industrial processes. Prominent examples include alkene polymerization, hydroformylation, alchohol carbonylation, alkene metathesis, hydrogenation, *et al*. Professor Paolo Chini's contributions to organometallic chemistry range from producing the first samples of isotactic polypropylene to pioneering the chemistry of metal carbonyls and their clusters. This presentation focuses on two of the major industrial applications of homogeneous, transition metal catalysts: alkene polymerization and hydroformylation. Catalytic polymerization with homogeneous systems enables increasingly sophisticated processes, such as the Dow Chain–Shuttling technology that produces blocky alkene co-polymers with unusual properties on a commodity scale. Ultimately, the composition and structure of such blocky copolymers are kinetically controlled. Key to revealing fundamental kinetic and mechanistic data concerning "Chain–Shuttling" is the development and implementation of a chromophore quench-labeling strategy; such experiments reveal catalyst active site counts and enable detailed extraction of propagation and chain-transfer kinetics from the evolution of polymer molecular weight distributions.



Alkene hydroformylation as catalyzed by metal carbonyls yields nearly 10 million metric tons of linear, achiral aldehyde per annum. New ligands, such as BisDiazaPhospholanes (BDPs), combine with common Rh-precursors to provide high rates, regioselectivity that favors the branched isomer, and high enantioselectivity. These qualities open new possibilities for atom–economical production of complex organic molecules. But what controls the selectivity? Insight results from operando NMR studies in the Wisconsin High Pressure NMR Reactor (WiHP-NMRR). Monitoring catalyst speciation, reaction rates, and reaction selectivity simultaneously, provides quantitative data for detailed kinetic analysis that reveals intimate details of the reaction mechanism and the origins of selectivity under a variety of reaction conditions.

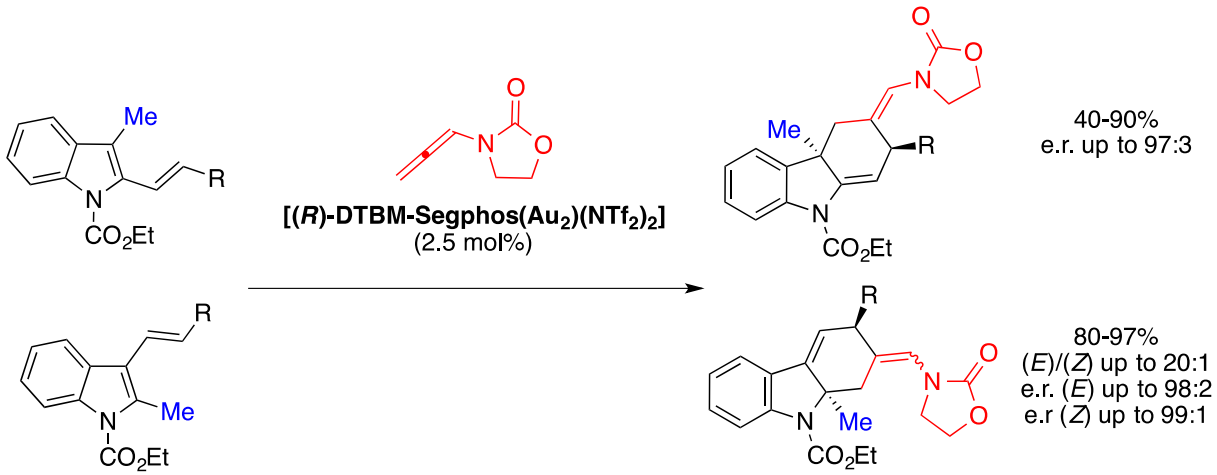


Gold(I)-catalyzed [4+2] cycloaddition reactions of vinylindoles and allenes

Valentina Pirovano[a], *Elisabetta Rossi*[a], *Giorgio Abbiati*[a]

[a] *DiSFarm - Sezione Chimica Generale e Organica "A. Marchesini", Università degli Studi di Milano, Via G. Venezian 21, 20133 Milano, Italy; valentina.pirovano@unimi.it*

Carbazole and tetrahydrocarbazole rings are the key structural motif in a great number of biological active molecules, including natural alkaloids and synthetic products.(1) For this reason, strategic syntheses of these indole derivatives are highly required, in particular when based on asymmetric methodologies. In this research field, 2- and 3-vinylindoles have become versatile 4C building blocks for the synthesis of complex tetrahydrocarbazole derivatives by means of [4+2] cycloadditions.(2) Among dienophiles, it has been shown that gold activated allenes could participate in [4+2] processes(3) and we published the first example of gold catalyzed reaction of 2- and 3-vinylindoles with allenamides(4) and allenyl esters.(5) In this latter work we reported also some preliminary investigations on enantioselective synthesis of tetrahydrocarbazoles, by conducting the reaction in the presence of a chiral gold(I) phosphoramidites. Prompted by these results and taking into account the importance of asymmetric tetrahydrocarbazole synthesis, we next explored the reactivity of 3/2-substituted-2/3-vinylindoles with *N*-allenamides under chiral gold(I) catalysis for the synthesis of a new series of dearomatized indoles bearing a quaternary C4a/C9a stereocenter (Scheme 1).(6) The results obtained in this work will be presented in the context of our investigations on gold(I) catalyzed syntheses of tetrahydrocarbazoles.



References: (1) A. W. Schmidt, K. R. Reddy, H.-J. Knölker, *Chem. Rev.* **2012**, *112*, 3193; A. Głuszyńska, *Eur. J. Med. Chem.* **2015**, *94*, 405; L. S. Tsutsumi, D. Gundisch, D. Sun, *Curr. Top. Med. Chem.* **2016**, *16*, 1290. (2) U. Pindur, *Heterocycles* **1988**, *27*, 1253; R. F. Kester, S. J. Berthel, F. Firooznia, *Top. Heterocycl. Chem.* **2010**, *26*, 327. (3) Y. Li, W. Li, J. Zhang, *Chem. Eur. J.* **2017**, *23*, 467; F. López, J. L. Mascareñas, *Chem. Soc. Rev.* **2014**, *43*, 2904. (4) V. Pirovano, L. Decataldo, E. Rossi, R. Vicente, *Chem. Commun.* **2013**, *49*, 3594. (5) V. Pirovano, E. Arpini, M. Dell'Acqua, R. Vicente, G. Abbiati, E. Rossi, *Adv. Synth. Catal.* **2016**, *358*, 403. (6) V. Pirovano, M. Borri, G. Abbiati, S. Rizzato, E. Rossi, *Adv. Synth. Catal.* **2017**, accepted, DOI: 10.1002/adsc.201700280.

Hydrogen and chemicals from renewable alcohols by Organometallic Electro-Reforming (OMER)

Marco Bellini[a], *Maria V. Pagliaro*[a,b], *Hamish A. Miller*[a], *Werner Oberhauser*[a], *Maria G. Folliero*[a], *Andrea Marchionni*[a], *Jonathan Filippi*[a], *Francesco Vizza*[a] *and Hansjörg Grützmacher*[c].

[a] *Istituto di Chimica dei Composti Organometallici – Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019, Sesto Fiorentino (Firenze);* [b] *Dipartimento di Chimica, Università degli Studi di Siena, Via Aldo Moro 2, 53100 Siena;* [c] *Department of Chemistry and Applied Biosciences, ETH Hönggerberg, CH-8093 Zurigo, Svizzera. marco.bellini@iccom.cnr.it*

The production of hydrogen by electrolysis of water is a well-established technology but it does not have a significant commercial impact due to its high energy cost.
A recent strategy for reducing the energy cost of electrolytic hydrogen production involves the replacement of water oxidation at the anode of the electrolytic cell with the oxidation of a soluble substrate, like a bioalcohol, whose oxidation potential is much lower than that of water. This leads to a significant reduction of the potential required to produce hydrogen (1). The original idea presented here, consists in coupling the partial oxidation of renewable alcohols promoted by an organometallic complex [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] (trop$_2$NH=bis(5-H dibenzo[a,d]cyclohepten-5-yl)-amine; OTf- = CF_3SO_3- = triflate; (see 1@C in figure 1 for a structure plot) with the cathodic hydrogen evolution reaction (2). We report an electrolytic device that achieves the simultaneous selective production of carboxylate compounds and high-purity hydrogen gas. This electrolyzer, that we call OrganoMetallic ElectroReformer (OMER), in contrast to electrolysis technologies based on nanoparticles, offers potentially enormous advantages as in principle every single metal atom is catalytically active, thus allowing a vastly reduced metal loading. At the same time, this technology is capable of providing simultaneously high levels of pure hydrogen production and chemicals of industrial importance by the exploitation of bioalcohols. The absence of oxygen production in the anode compartment facilitates the production of hydrogen at elevated pressures. Consequently, we hypothesize the exploitation of bioalcohol electroreforming as an essential component of the biorefinery platform using this new class of electrolyzers based on organometallic complexes.

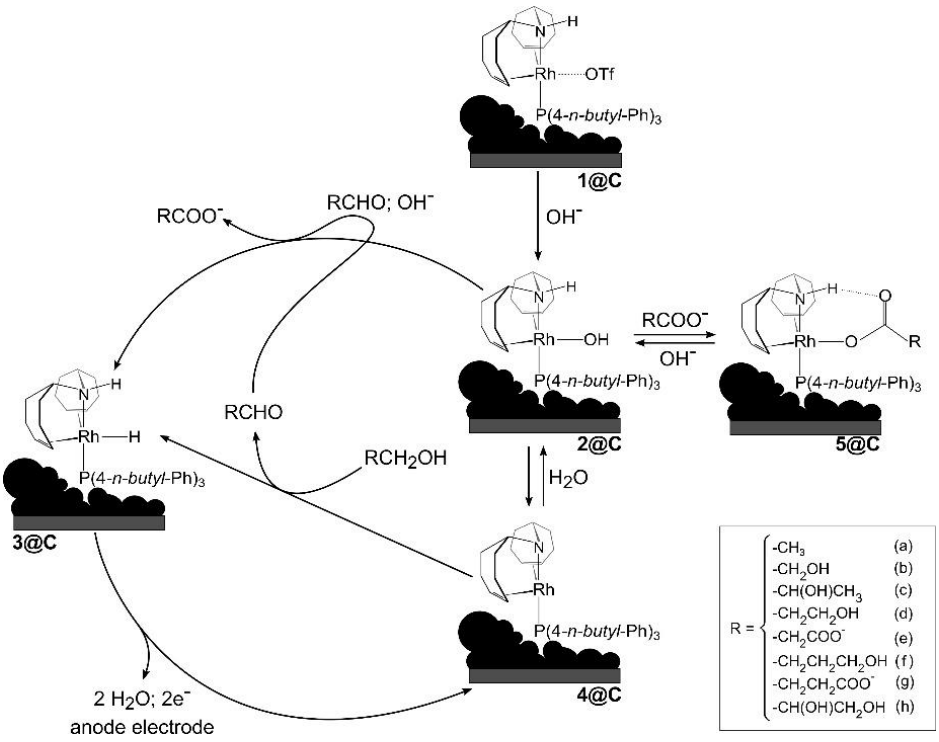


Figure 1: proposed mechanism for the reactions occurring on the anode coated with 1@C.

References: 1. F.Vizza et al., Nat. Comm. 5, 4036 (2014). 2. M. Bellini et al., ChemCatChem 9, 746 (2017).

Conferenze Plenarie

- INO PL01: Jeroen A. van Bokhoven, Institute for Chemical and Bioengineering, ETHzurich and Laboratory for Catalysis and Sustainable Chemistry, ENE Division, Paul Scherrer Institute, Villigen
- INO PL02: Paolo Carloni, Forschungszentrum Jülich, Jülich, Germany and Department of Physics, RWTH-Aachen University, Aachen, Germany

Action at a distance: observing hydrogen spillover

Jeroen A. van Bokhoven

Institute for Chemical and Bioengineering, ETHzurich and Laboratory for Catalysis and Sustainable Chemistry, ENE Division, Paul Scherrer Institute, Villigen; j.a.vanbokhoven@chem.ethz.ch, jeroenvanbokhoven@psi.ch

Depending on the nature of the support, hydrogen spillover may occur in hydrogen-catalyzed reactions. Evidence of its occurrence on non-reducible supports, such as alumina, is disputed while its occurrence on reducible supports like titania is generally accepted. [1] Direct experimental proof of its existence does not exist due the lack of well-defined model systems and the inability to observe the effect directly. We employ enhanced precision of top-down nanofabrication [2-4] and single-particle in-situ X-ray absorption spectromicroscopy [3,4] to visualize hydrogen spillover. For the first time, distance dependence of hydrogen spillover has been experimentally visualized [4], and the hydrogen diffusion and migration mechanisms are elucidated by DFT calculations.
We develop a novel model surface with precision in particle size and its positioning. Multiple pairs of nano-sized iron oxide and platinum particles, at varying distances from each other starting at 0 nm to 45 nm, are positioned on the same support with an accuracy of one nanometer. X-ray photoemission electron microscope (XPEEM) at the Swiss Light Source (SLS) enables in-situ structural analysis on individual iron oxide particles to visualize chemical reduction by hydrogen spillover at different distances [4]. We find that spillover on alumina support depends on distance from the catalyst and is relevant only at distances below 15 nm, occurring on three-coordinate aluminum sites. Spillover on titania support occurs via coupled electron-proton transfer and is uniform all over the support irrespective of distance.

[1] R. Prins, *Chemical Reviews* **112** (2012) 2714.
[2] W. Karim, S. A. Tschupp, M. Oezaslan, T. J. Schmidt, J. Gobrecht, J. A. van Bokhoven, and Y. Ekinci, *Nanoscale* **7** (2015) 7386
[3] W. Karim, A. Kleibert, U. Hartfelder, A. Balan, J. Gobrecht, J. A. van Bokhoven, and Y. Ekinci, *Scientific Reports* **6** (2016) 18818.
[4] W. Karim, S. Clelia, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, and J. A. van Bokhoven, *Nature* **541** (2017) 68.

Multiscale simulation-based structural predictions of metalloproteins of pharmacological relevance.

Paolo Carloni,

Forschungszentrum Jülich, Jülich, Germany and Department of Physics, RWTH-Aachen University, Aachen, Germany
p.carloni@fz-juelich.de

I will present recent hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) - based investigations of the structural determinants of the drug cisplatin in complex with some of its cellular targets. This information may be of help in counteracting drug's resistance, which limits greatly drug's efficacy after repeated administrations. The talk will close with a QM/MM study on a bioinorganic system of possible neuropharmacological interest, copper binding to the human alpha synuclein protein.

Funding: HPC-Leap, BioExel, Human Brain Project, DFG.

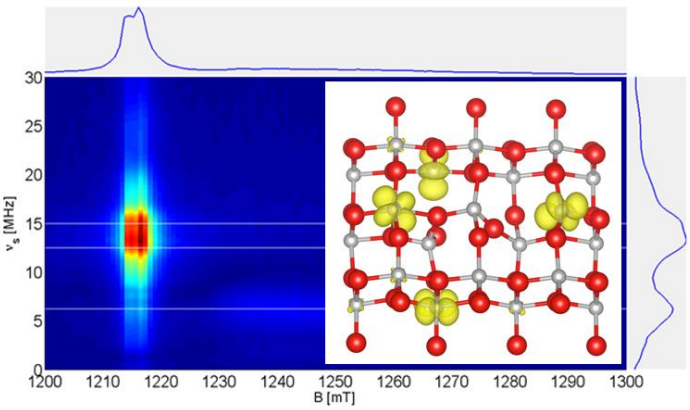
Keynote e Conferenze su invito

- INO KN 01: M. Chiesa, Università di Torino
- INO KN 02: M. Ravera, Università del Piemonte Orientale
- INO KN 03: R. Zanoni, Università degli Studi di Roma "La Sapienza"
- INO KN 04:L. Monsù, Università di Messina
- INO KN 05: L. Zaccaro, CNR, Napoli - Università di Napoli ''Federico II''
- INO KN 06: F. Ragaini, Università degli Studi di Milano
- INO KN 07: D. Armentano, Università della Calabria
- INO KN 08: C. Tubaro, Università degli Studi di Padova
- ORG/INO KN 01: A. Caselli, Università degli Studi di Milano - ISTM-CNR, Milano
- ORG/INO KN 02: Lorenzo Zani, CNR, Sesto Fiorentino (Fi)
- INO IL 01: Andrew J. T. Shore-Royal Society of Chemistry, Cambridge (UK)
- TEO/INO KN 01: B. Civalleri, Università di Torino
- TEO/INO KN 02: N. Re, Università "G. D'Annunzio" Chieti-Pescara

Exploring and Engineering Spin-states in Solid State and Surface Chemistry

Mario Chiesa

Dipartimento di Chimica Università di Torino, Via Giuria 7, 10125 Torino E-mail mario.chiesa@unito.it



Spin is a fundamental property of elements and molecules, which originates from the presence of unpaired electrons. Spin states constitute thus a fundamental aspect of the electronic structure, which concur to determine the electronic, magnetic and chemical properties of matter. Moreover, the possibility to control the spin-dependent electronic structure of molecular-scale architectures is essential for the development of solid-state devices and the implementation of future devices based on quantum states. The determination and control of spin states is thus an important - and often not properly discussed – issue in the context of understanding many aspects of chemical reactivity and materials science. Electron Pramagnetic Resonance (EPR) spectroscopy is the technique of election for this task, allowing for a molecular level description of the structure and reactivity of paramagnetic species. In this contribution, an overview of the wealth and breadth of information that can be obtained from EPR in the characterization of paramagnetic species in the bulk or at the surface of solid-state systems will be provided. Attention will be paid to illustrate the advantages offered by modern pulsed EPR methodologies in determining the spin state and monitoring the elementary processes occurring within the coordination sphere of paramagnetic species, with emphasis on transition-metal ions (TMI). Specific cases involving TMI acting as spin bearing units will be presented, trying to outline the methodological approaches, which characterize the application of advanced EPR techniques and the questions that can be answered and addressed in connection to the chemical reactivity and magnetic properties of solid state systems.

References:

1. Maurelli, S., Vishnuvarthan, M., Chiesa, M., Berlier, G., Van Doorslaer, S. Elucidating the Nature and Reactivity of Ti Ions Incorporated in the Framework of AlPO-5 Molecular Sieves. New Evidence from ^{31}P HYSCORE Spectroscopy *J. Am. Chem. Soc.*, 2011, 133, 7340.
2. Morra, E., Giamello, E., Van Doorslaer, S., Antinucci, G., D'Amore, M., Busico, V. and Chiesa, M. Probing the Coordinative Unsaturation and Local Environment of Ti^{3+} Sites in an Activated High-Yield Ziegler–Natta Catalyst. *Angew. Chem. Int. Ed*., 2015, 54, 4857.
3. Atzori, M., Morra, E, Tesi, L., Albino, A., Chiesa, M., Sorace, L., Sessoli R. Quantum Coherence Times Enhancement in Vanadium(IV)-based Potential Molecular Qubits: the Key Role of the Vanadyl Moiety *J. Am. Chem. Soc.*, 2016, 138, 11234.
4. Chiesa M. Livraghi, S., Giamello, E. Albanese, E. Pacchioni G. Ferromagnetic Interactions in Highly Stable, Partially Reduced TiO_2: The S=2 State in Anatase *Angew. Chem. Int. Ed.* 2017, 56, 2604.

Dual-targeting hybrid anticancer platinum(IV) prodrugs for combination therapy

Mauro Ravera

Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale T. Michel 11, 15121 Alessandria, Italy; mauro.ravera@uniupo.it.

Despite the use of cisplatin (CDDP) and its Pt(II) congeners in several chemotherapeutic regimes, the associated heavy side effects and the intrinsic/acquired chemoresistance have prompted inorganic medicinal chemists to design, *inter alia*, alternative Pt(IV) derivatives.
These antitumor complexes are considered prodrugs, since they can be selectively reduced in the hypoxic and acidic intracellular milieu of the tumor cells to the corresponding cytotoxic Pt(II) metabolite with the usual loss of their two axial ligands (*activation by reduction*, Figure 1).

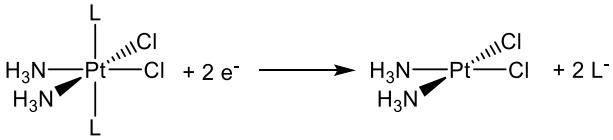


Figure 1

The saturated six-coordinated octahedral geometry of the low spin d^6 Pt(IV) is characterized by a high kinetic inertness that minimizes off-target effects, thus improving the therapeutic index and, furthermore, allowing oral administration.
Their axial ligands affect the cellular accumulation of Pt(IV) compounds due to their enhanced lipophilicity (the influx occurs mainly by passive diffusion). Moreover, these axial ligands can be biologically active vectors towards tumor tissue or adjuvant (synergistic) drugs. Indeed, clinicians usually combine the approved Pt(II) drugs with other therapeutics to potentiate their efficacy. The *bifunctional* (dual action) Pt(IV) derivatives, where one/two synergistic drug molecules are conjugated to Pt(IV) in the axial position/s, represent an efficient tool to realize such a combination therapy (Figure 2) (1).

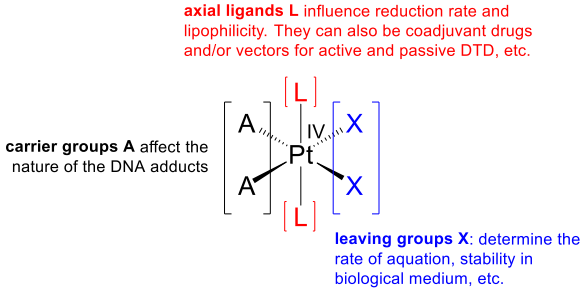


Figure 2

Several examples will be described. In particular, there is a growing interest in the co-administration of DNA-damaging drugs (including CDDP) with Histone DeACetylase inhibitors (HDACi) as auxiliary agents. The naïve rationale for such a combination is that the inhibition of HDAC results in the hyperacetylation of lysines in nucleosomal histones that no longer associate with the nuclear DNA. This increases the accessibility of nucleobases to the DNA-damaging agents, as CDDP (2-4).

References:
1. E. Gabano, M. Ravera, D. Osella, Dalton. Trans 43 (2014) 9813.
2. M. Alessio, I. Zanellato, I. Bonarrigo, E. Gabano, M. Ravera, D. Osella, J. Inorg. Biochem. 129 (2013) 52.
3. M. Ravera, E. Gabano, I. Zanellato, A. Gallina, E. Perin, A. Arrais, S. Cantamessa, D. Osella, Dalton Trans. 46 (2017) 1559.
4. V. Novohradsky, L. Zerzankova, *et al.*, J. Inorg. Biochem. 140 (2014) 72; Biochem. Pharmacol. 95 (2015) 133.

Highly delocalized stable systems on semiconductor surfaces

Robertino Zanoni

Dipartimento di Chimica, Università degli Studi di Roma La Sapienza, piazzale Aldo Moro, 5, I-00185 Roma; Robertino.zanoni@uniroma1.it

The quest for systems able to bring the field of molecular-scale electronics into true applicability has started since few decades now, but the challenging key issue of their stability still requires continuous effort.(1) The exciting electronic, mechanical, thermal, and optical properties of graphene have switched on areas of basic and applied research in many fields worldwide.(2) The relatively recent progresses in the characterization of true graphene deposits have allowed a much better interpretation of results in the field, also allowing for a comparison between the outcomes of distinct synthetic strategies.(3) A notable goal in view of studies and applications of graphene is the obtainment of handy forms of this material, allowing for developments in real conditions. To achieve applications, a large-scale production of high quality graphene sheets in an efficient and effective way is required.(4)

In this lecture, very recent results will be discussed coming from research done at the Department of Chemistry, La Sapienza, which stem from an international collaboration work with E.A. Dalquiele (Univ. of Montevideo), R. Schrebler (Univ. Valparaiso), A.G. Marrani (Un. La Sapienza).(5)

Novel experimental approaches to produce graphene/silicon interface will be reported, which consist of an electrochemical reduction of graphene oxide (GO) directly in contact with Si(111) wafers. Such modified surface was utilized as a working electrode in an electrochemical cell, and characterized also by means of field-emission scanning electron microscopy, and Raman and X-ray photoelectron spectroscopies. The transformation of GO into electrochemically reduced graphene oxide (ERGO) over the silicon surface was fully demonstrated. Parallel research studies on the functionalization of graphene nanoplatelets (GNP) with substituted porphyrins in a collaboration with P. Tagliatesta (Univ. Tor Vergata) and S. Bellucci (INFN) will be also reported.

These outcomes are new and a step forward in the direction of an easy procedure to high quality graphene interfaces.

References: 1. M. Ratner, Nat. Nanotechnol. 8, 378–381 (2013). 2. Ray, S. C. Applications of Graphene and Graphene-Oxide Based Nanomaterials; William Andrew Publishing: Oxford, 2015; pp 1−38. 3. A.C. Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; et al., Phys. Rev. Lett. 97, 187401 (2006). 4..T. Kuila, S. Bose, A.K. Mishra, P. Khanra, N.H. Kim, J.H. Lee, Prog. Mater. Sci. 57, 1061−1105 (2012). 5. E.A. Dalquiele, A.G. Marrani, R. Zanoni, Journal of Physical Chemistry C 121, 5675-5683 (2017).

On the chirality in porphyrin nanoassemblies

Luigi Monsù Scolaro

Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina and C.I.R.C.M.S.B; e.mail: lmonsu@unime.it

Observation of optical activity for assemblies of achiral entities in the absence or in the presence of chiral templates has attracted attention of many researchers, due to the potential implications with the ubiquitous homochirality in our universe. Some porphyrins have been of quite considerable importance for such studies due to their ability to self-assemble into chiral supramolecular structures. In this contribution, a series of examples will be reported on cationic and anionic water soluble porphyrins.

Under moderate ionic strength conditions, a copper(II) metal complex of a cationic porphyrin (t-CuPagg) extensively self-aggregates forming large mesoscopic clusters that bind avidly polyanionic substrates such as poly-glutamate (PGA). This interaction leads to large enhancement of the induced circular dichroism signals in the absorption region of the porphyrin, through a specific chirality transfer mechanism.(1) Such an effect could be exploited as chiroptical probe towards simple chiral substrates (carbohydrates or nucleotides) and biopolymers such as human serum albumin, poly(adenylic acid), calf-thymus DNA and alginate.(2)

Under proper conditions, an anionic porphyrin (TPPS) self-assembles into nanotubes, that in the absence of any added chiral templating agent, show an unpredictable chirality. We provided evidence that the rate of aggregation plays an important role on the final observed optical activity.(3) The supramolecular aggregation processes are based on thermodynamically- and kinetically-controlled paths related to medium properties and experimental conditions such as concentration, pH and ionic strength. Also the important role of mixing protocol, counter-anions(4) and isotopic substitution(5) on kinetics and chirality will be discussed. In the presence of chiral templating reagents, such as tartaric acid, distinct kinetic patterns and a corresponding variance in the amplification of chirality has been also observed for the two enantiomers.(6) The resulting chiral nanoaggregates have been efficiently transferred onto solid substrates by soft lithography.(7) Quite recently, control of the handedness of chiral J-aggregates obtained from such achiral compounds has been achieved by applying rotational, gravitational and orienting forces at the beginning of the assembly process.(8)

References: 1. Occhiuto I.; De Luca G.; Villari V.; Romeo A.; Micali N.; Pasternack R. F.; Monsù Scolaro L. *Chem. Commun.*, **2011**, *47*, 6045. 2. Occhiuto, I.G.; Samperi, M.; Trapani, C.; De Luca, G.; Romeo, A.; Pasternack, R.F.; Scolaro, L.M. *J. Inorg. Biochem*. **2015**, *153*, 361. 3. Romeo, A.; Castriciano, M. A.; Occhiuto, I.; Zagami, R.; Pasternack, R. F.; Scolaro, L. M. *J. Am. Chem. Soc*. **2014**, *136*, 40. 4. Occhiuto, I.G.; Zagami, R.; Trapani, M.; Bolzonello, L.; Romeo, A.; Castriciano, M.A.; Collini, E. Scolaro, L.M. *Chem. Commun*. **2016**, *52*, 11520. 5. Zagami, R. Romeo, A.; Castriciano, M.A.; Scolaro, L.M. *Chem. Eur. J* **2017**, *23*, 70. 6. Castriciano, M. A.; Romeo, A.; Zagami, R.; Micali, N.; Scolaro, L. M. *Chem. Commun*. 2012, 48, 4872. 7. Castriciano, M.A.; Gentili, D.; Romeo, A. Cavallini, M.; Scolaro L. M. *Scientific Reports* **2017**, *7*, 44094. 8. Micali, N.; Engelkamp, H.; van Rhee, P. G.; Christianen, P. C. M.; Scolaro, L. M.; Maan, J. C. *Nat Chem* **2012**, *4*, 201.

RGDechi chimeric peptide as new scaffold for gaining insight into structural features of integrins selectivity for theranostics.

Laura Zaccaro[a,b], *Annarita Del Gatto*[a,b], *Luigi Russo*[c], *Biancamaria Farina*[a], *Annamaria Liguoro*[a], *Sonia Di Gaetano*[a,b], *Domenica Capasso*[d], *Daniela Comegna*[a], *Roberto Fattorusso*[c], *Michele Saviano*[b,e],

[a]*Institute of Biostructures and Bioimaging-CNR, Via Mezzocannone 16, 80134, Naples, Ital;* [b]*Interdepartmental Center of Bioactive Peptide, University of Naples ''Federico II'', Via Mezzocannone 16, 80134 Naples, Italy;* [c]*Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples, via Antonio Vivaldi 43, 81100 Caserta, Italy;* [d]*Department of Pharmacy, University of Naples ''Federico II'',Via Mezzocannone 16, 80134 Naples, Italy;* [e]*Institute of Crystallography-CNR, Via Amendola 122/O, 70126 Bari, Italy. lzaccaro@unina.it*

Over the last three decades intensive efforts have been devoted to elucidate the structural features that govern integrin-specific interactions. Given the involvement of integrins in the regulation of physiological processes (1), as well as of pathological ones, the development of integrin subtype-exclusive antagonists is highly desirable.

Integrins $\alpha_v\beta_3$, $\alpha_v\beta_5$ and $\alpha_5\beta_1$, key mediators of cell adhesion, differentiation, proliferation, angiogenesis and tumor growth, have been considered very promising targets for theranostic application. Due to the similarity of the RGD binding regions in these integrins, the development of small synthetic molecules with high activity and selectivity for the different subtypes is a tricky goal to pursue. The majority of the ligands described so far as integrin subtype-selective have in fact residual, yet significant, affinity for the other integrins, thus stimulating extensive research to develop novel integrin specific molecules.

In the last decade we designed and characterized the peptide RGDechi, a chimeric molecule encompassing a cyclic portion containing the RGD triade for integrin binding and a linear sequence derived from the C-terminal fragment of the echistatin protein to confer specificity for β_3 subunit (2). We demonstrated anti-adhesive and proapoptotic effects on tumor cells and antiangiogenic activity in vivo (3,4,5). More, SPECT and PET imaging studies with ^{111}In and ^{18}F-labelled RGDechi in a xenograft model confirmed the ability of peptide to selectively visualize this integrin. Recently NMR and computational analyses on cell membranes allowed a detailed understanding of $\alpha_v\beta_3$/RGDechi recognition mechanism (6). On the basis of the identified molecular determinants, we used RGDechi as scaffold peptide gaining from its chimeric nature to shift the selectivity towards $\alpha_v\beta_5$ or $\alpha_5\beta_1$ integrins.

In conclusion our studies, providing an improved understanding of ligand–integrin interactions, pave the way for the design of novel peptides selective for the different integrins to use in theranostics.

References: 1. Mould AP, Humphries MJ. Cell biology: adhesion articulated. *Nature* **432**, 27, 10.1038/432027a (2004). 2. Del Gatto, A. *et al.* Novel and selective alpha(v)beta3 receptor peptide antagonist: design, synthesis, and biological behavior. *J Med Chem* **49**, 3416-3420, doi:10.1021/jm060233m (2006). 3 Zannetti, A. *et al.* Imaging of alpha(v)beta(3) expression by a bifunctional chimeric RGD peptide not cross-reacting with alpha(v)beta(5). *Clin Cancer Res* **15**, 5224-5233, doi:10.1158/1078-0432.CCR-08-3270 (2009). 4. Santulli, G. *et al.* Evaluation of the anti-angiogenic properties of the new selective alphaVbeta3 integrin antagonist RGDechiHCit. *J Transl Med* **9**, 7, doi:10.1186/1479-5876-9-7 (2011). 5. Pisano, M. *et al.* In vitro activity of the alphavbeta3 integrin antagonist RGDechi-hCit on malignant melanoma cells. *Anticancer Res* **33**, 871-879 (2013). 6.Farina B, et al. A Combined NMR and Computational Approach to Determine the RGDechi-hCit-αvβ3 Integrin Recognition Mode in Isolated Cell Membranes. Chemistry **22**, 681-693, doi: 10.1002/chem.201503126 (2016).

Schiff Bases of the BIAN Family: from Symmetrical Biaryl Derivatives to Mixed, Alkyl, Chiral or Reduced Ligands and Heterogeneous Catalysts.

Fabio Ragaini

Università degli Studi di Milano, Dipartimento di Chimica; E-mail: fabio.ragaini@unimi.it

The number of applications of *bis*-imines as ligands in homogeneous catalysis has much increased in recent years. Derivatives of acenaphthenequinone (R-BIANs) are especially useful to this purpose because the rigidity of the acenaphthene skeleton strengthen coordination to a metal and add stability against the rupture of the central C-C bond of the diimine moiety.

During the years, we have expanded the available range of Ar-BIANs to ligands where the aryl group bears strongly electronwithdrawing substituents (1), two different aryl groups are present (2), and first prepared usually unstable Alkyl-BIAN compounds (3,4). The key principles which allowed these products to be obtained will be illustrated. Solubility of the products and the right control of ring strain for alkyl derivatives are essential points.

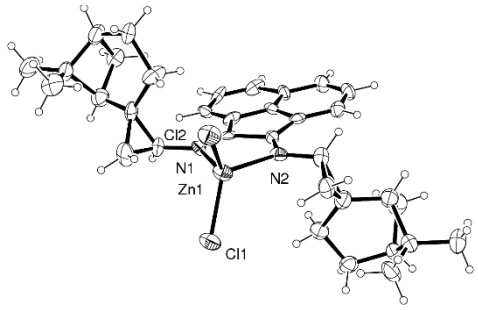


Figure 1

The coordinating strength of a series of Ar-BIAN ligands to several palladium complexes has been measured and varies linearly with the log of Hammett σ constant. The slope of the correlation (ρ) depends on the metal complex and can be regarded as measure of its Lewis acidity (5).

The family of R-BIAN ligands was then further expanded to chiral derivatives (6) (Figure 1) and finally to reduced ligands, Ar-BIANH_2 (7) (Figure 2). The latter are air sensitive compounds, but are stable under in the solid state an inert atmosphere and can be employed to synthesize catalytically active complexes without resorting to the use of reduced metal precursors or alkaline-metal reduced intermediates (8).

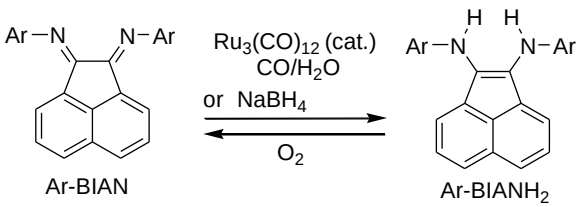


Figure 2

At the end of this evolution, the last application was to decompose the coordinated ligand at high temperatures to generate heterogeneous nitrogen- enriched graphitic cobalt catalysts, effective in hydrogenation reactions for which traditional cobalt catalysts are inactive (9).

References:
1. M. Gasperini, F. Ragaini, S. Cenini *Organometallics*, **2002**, *21*, 2950.
2. M. Gasperini, F. Ragaini, E. Gazzola, A. Caselli, P. Macchi *Dalton Trans.*, **2004**, 3376.
3. F. Ragaini, M. Gasperini, E. Gallo, P. Macchi *Chem. Commun.*, **2005**, 1031.
4. F. Ragaini, M. Gasperini, P. Parma, E. Gallo, N. Casati, P. Macchi *New J. Chem.* **2006**, *30*, 1046.
5. M. Gasperini, F. Ragaini *Organometallics* **2004**, *23*, 995.
6. M. Hagar, F. Ragaini, E. Monticelli, A. Caselli, P. Macchi, N. Casati, *Chem. Commun.* **2010**, *46*, 6153.
7. M. Viganò, F. Ferretti, A. Caselli, F. Ragaini, M. Rossi, P. Mussini, P. Macchi, *Chem. Eur. J.* **2014**, *20*, 14451.
8. A. Cimino, F. Moscatelli, F. Ferretti, F. Ragaini, S. Germain, J. Hannedouche, E. Schulz, L. Luconi, A. Rossin, G.Giambastiani, *New J. Chem.* **2016**, *40*, 10285.
9. D. Formenti, F. Ferretti, C. Topf, A.-E. Surkus, M.-M. Pohl, J. Radnik, M. Schneider, K. Junge, M. Beller, F. Ragaini, *J. Catal.* **2017**, *351*, 79.

Synthesis and X-ray Snapshots of Ultrasmal Metallic Clusters within Metal-Organic Frameworks for High Performance in Catalysis.

D. Armentano[a], *E. Pardo*[b], *A. Leyva–Pérez*[c], *A. Corma*[c]

[a]*Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87030 Rende, Cosenza, Italy;* [b]*Departament de Química Inorgànica, Instituto de Ciencia Molecular (ICMOL), Universitat de València, 46980 Paterna, València, Spain;* [c]*Instituto de Tecnología Química (UPV–CSIC), Universidad Politècnica de València–Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, 46022 Valencia, Spain; Email:donatella.armentano@unical.it*

Cluster catalysis may represent a major technological step forward in a similar way to that metal nanoparticles did, in view of the extremely high catalytic performance of metal clusters below the nanometer. However, much effort is still needed in terms of synthesis, stabilization and characterization of such small entities in order to design precisely novel catalysts bearing such active sites. Ultrasmall metal nanoclusters (NCs),(*1*) consisting of aggregations of less than 10 atoms with a high percentage of them exposed to the external environment, have emerged as formidable catalysts capable to surpass the *state-of-the-art* catalysts in organic reactions of industrial interest, being thus capable to make feasible certain reactions which are currently financially prohibitive. Such small NCs, that may give rise to a technological leap in a similar way as the irruption of metal nanoparticles (NPs) did, still show important weaknesses regarding the synthetic control of their shape and nuclearity as well as their lack of stability.(*2*) Supporting these clusters within a type of porous materials named metal-organic frameworks (MOFs) is a very promising strategy. Metal-Organic Frameworks (MOFs), a type of porous materials possessing regular and well-defined channels and exhibiting a fascinating host-guest chemistry,(*3*) are, in principle, the perfect platforms to synthesize, in a controlled manner, metal clusters below the nanometer allowing to gain information about their nature by means of X–ray crystallography, thus illustrating every single step during their synthetic route.(*4*) Here we report on the MOF-mediated chemical synthesis of structurally and electronically well–defined ultrasmall Pt_2 (Fig. 1) and $[Pd_4]^{2+}$ clusters, grown within the functional channels of MOFs specifically designed for this purpose.(*4-6*) The functional pores, a metal controlled stoichiometry and a highly homogeneous distribution of the metal ions results in such controlled chemical synthesis. Reactions in which the resulting $[Pd_4]^{2+}$– and Pt_2–MOF hybrid material outperform *state–of–the–art* metal catalysts will be illustrated.

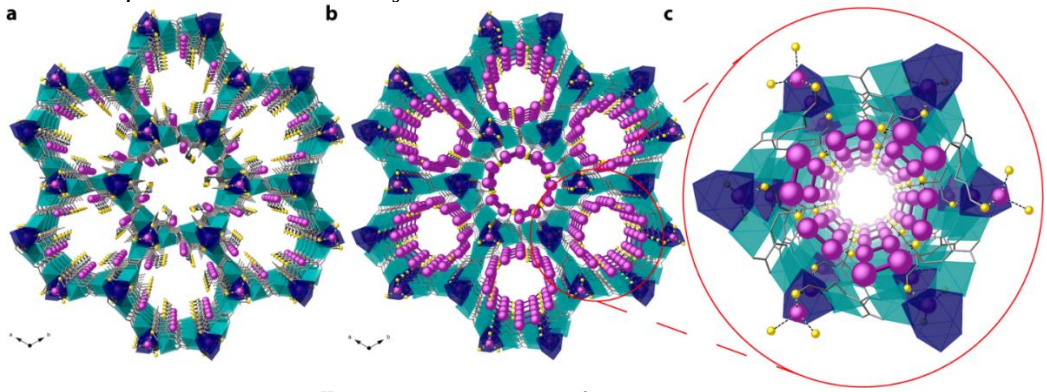


Fig. 1. Crystal structures of the Pt^{II}@MOF (**a**) and Pt_2^0@MOF (**b**). **c**. Perspective view, in detail, of a channel of Pt_2^0@MOF along the *c* axis. Cyan and blue polyhedral for Copper and calcium atoms, respectively, sticks for organic ligands. Dashed lines represent the Pt···S interactions.

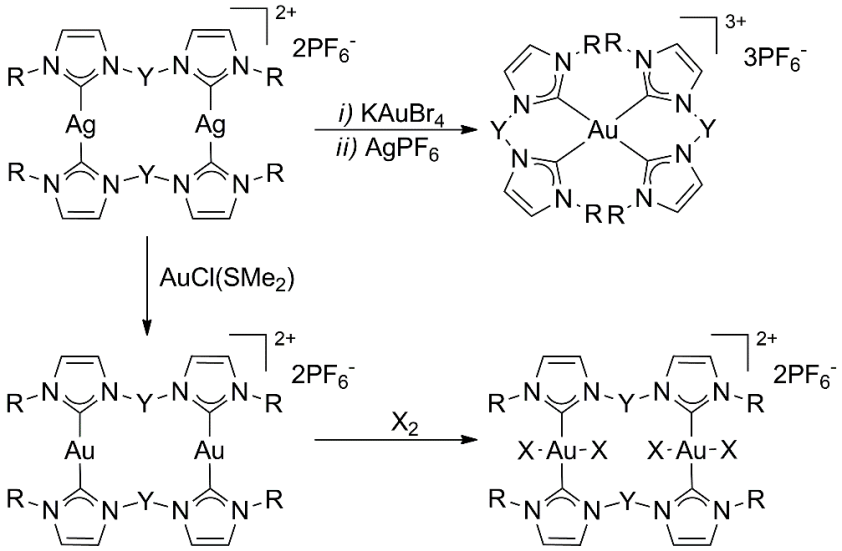
References: 1. A. Corma *et al.*, *Nat. Chem.* **5**, 775–781 (2013). 2. Y. Lei *et al.*, *Science (80-.).* **328**, 224–228 (2010). 3. M. O'Keeffe, O. M. Yaghi *et al.*, *Science (80-.).* **341**, 974 (2013). 4. A. Corma, A.Leyva-Perez, D. Armentano, E. Pardo *et al.*, *Nat. Mater.* DOI 10.1038/NMAT4910 (2017). 5. A. Leyva-Perez, D. Armentano, E. Pardo *et al.*, *J. Am. Chem. Soc.* **138**, 7864–7867 (2016). 6. D. Armentano, E. Pardo *et al.*, *Angew. Chem., Int. Ed.* **55**, 11167–11172 (2016).

Selective syntheses of mononuclear *vs* dinuclear gold(III) complexes with di(N-heterocyclic carbene) ligands

Cristina Tubaro[a], *Marco Baron*[a]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy.*
cristina.tubaro@unipd.it

N-heterocyclic carbene-gold species represent one of the most recent and appealing class of organometallic complexes, in view of their wide range of applications.(1) Limiting the attention to di(N-heterocyclic carbene) ligands, the synthesis of gold(I) complexes is quite straightforward and usually involves i) transmetalation of the carbene ligand from the corresponding silver(I) complex or ii) deprotonation of an azolium salt in the presence of a gold(I) species like $AuCl(SMe_2)$.(2)
By contrast, due to the instability of gold(III) towards reduction, deprotonation of an azolium salt in the presence of gold(III) precursors generally gives the corresponding gold(I) complex, so that transmetalation of the diNHC ligand remains the only viable synthetic procedure for diNHC-gold(III) species.(3) In this way mononuclear tricationic complexes are obtained with two diNHC ligands coordinated in a chelating fashion. Alternatively, bridged dinuclear gold(III) complexes can be prepared via oxidative addition of halogen X_2 (X=Cl, Br, I) to the pristine dinuclear gold(I) complexes.(4)
In this contribution, the different strategies for the synthesis of mononuclear or dinuclear gold(III) complexes with diNHC ligands will be illustrated and critically evaluated.
The different applications of the synthesized complexes will also be discussed.



References:
1. A. Biffis, M. Baron, C. Tubaro, *Adv. Organomet. Chem.* **2015**, *63*, 203.
2. (a) M. Baron, C. Tubaro, A. Biffis, M. Basato, C. Graiff, A. Poater, L. Cavallo, N. Armaroli, G. Accorsi, *Inorg. Chem.* **2012**, *51*, 1778. (b) C. Tubaro, M. Baron, M. Costante, M. Basato, A. Biffis, A. Gennaro, A. Ahmed Isse, C. Graiff, G. Accorsi, *Dalton Trans.* **2013**, *42*, 10952. (c) M. Baron, S. Bellemin-Laponnaz, C. Tubaro, B. Heinrich, M. Basato, G. Accorsi, *J. Organomet. Chem.* **2013**, *723*, 108. (d) M. Monticelli, C. Tubaro, M. Baron, M. Basato, P. Sgarbossa, C. Graiff, G. Accorsi, T. P. Pell, D. J. D. Wilson, P. J. Barnard, *Dalton Trans.* **2016**, *45*, 9540.
3. M. Baron, C. Tubaro, M. L. C. Cairoli, L. Orian, S. Bogialli, M. Basato, M. M. Natile, C. Graiff, *Organometallics*, in press.
4. M. Baron, C. Tubaro, M. Basato, A. A. Isse, A. Gennaro, L. Cavallo, C. Graiff, A. Dolmella, L. Falivene, L. Caporaso, *Chem. Eur. J.* **2016**, *22*, 10211.

Catalytic Applications of Pyridine-Containing Macrocyclic Complexes

Alessandro Caselli

Department of Chemistry, Università degli Studi di Milano and ISTM-CNR-Milano, Via Golgi 19, 20133 Milan, Italy. E-mail: alessandro.caselli@unimi.it

Polyazamacrocycles are a common class of macrocyclic compounds, utilized across a number of fields, including, but not limited to, catalysis, selective metal recovery and recycling, therapy and diagnosis, and materials and sensors.[1] Worth of note is their ability to form stable complexes with a plethora of both transition, especially late, and lanthanide metal cations.[2] Deviation of the macrocycle donor atoms from planarity often leads to rather uncommon oxidation states.[3] Both the thermodynamic properties and the complexation kinetics are strongly affected by the introduction of a pyridine moiety into the skeleton of polyazamacrocycles by increasing the conformational rigidity and tuning the basicity.[4] Pyridine-containing ligands engender great interest due to various potential field of applications. They have been successfully employed in biology, Magnetic Resonance Imaging, molecular recognition, supramolecular chemistry and self-assembly, molecular machines and mechanically interlocked architectures.[5] In this lecture, I will provide a perspective on the catalytic applications of metal complexes of pyridine-containing macrocyclic ligands (Pc-L's) which have been studied in our group (Figure), with a focus interest on the structural features relevant to catalysis.[6] The increased conformational rigidity imposed by the pyridine ring allowed for the isolation and characterization of metal complexes which showed a rich coordination chemistry.[7] The very different conformations accessible upon coordination and the easy tuneable synthesis of the macrocyclic ligands have been exploited in stereoselective syntheses.[8]

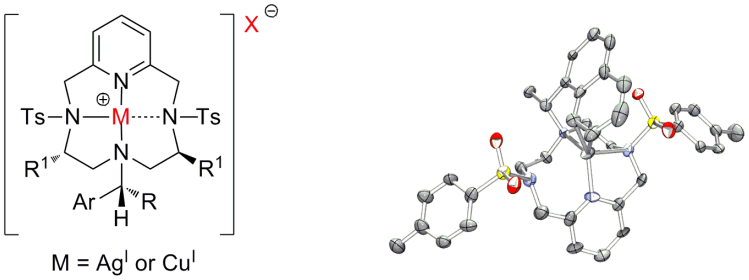


Figure. Metal complexes of Pc-L's and X-ray structure of a Cu(I) complex with a rare η^2-naphtyl moiety coordinated to the metal center.

Key words: macrocyclic ligands, homogeneous catalysis, copper, silver, C-C and C-O bond forming reactions.

References:

[1] L. F. Lindoy, G. V. Meehan, I. M. Vasilescu, H. J. Kim, J.-E. Lee, S. S. Lee, *Coord. Chem. Rev.* **2010**, *254*, 1713.

[2] T. Ren, *Chem. Commun.* **2016**, *52*, 3271.

[3] A. Casitas, X. Ribas, *Chem. Sci.* **2013**, *4*, 2301.

[4] K. M. Lincoln, M. E. Offutt, T. D. Hayden, R. E. Saunders, K. N. Green, *Inorg. Chem.* **2014**, *53*, 1406.

[5] M. Rezaeivala, H. Keypour, *Coord. Chem. Rev.* **2014**, *280*, 203.

[6] B. Castano, S. Guidone, E. Gallo, F. Ragaini, N. Casati, P. Macchi, M. Sisti, A. Caselli, *Dalton Trans.* **2013**, *42*, 2451.

[7] a) G. Tseberlidis, M. Dell'Acqua, D. Valcarenghi, E. Gallo, E. Rossi, G. Abbiati, A. Caselli, *RSC Adv.* **2016**, *6*, 97404; b) T. Pedrazzini, P. Pirovano, M. Dell'Acqua, F. Ragaini, P. Illiano, P. Macchi, G. Abbiati, A. Caselli, *Eur. J. Inorg. Chem.* **2015**, *2015*, 5089.

[8] a) M. Dell'Acqua, B. Castano, C. Cecchini, T. Pedrazzini, V. Pirovano, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* **2014**, *79*, 3494; b) M. Trose, M. Dell'Acqua, T. Pedrazzini, V. Pirovano, E. Gallo, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* **2014**, *79*, 7311; c) B. Castano, E. Gallo, D. J. Cole-Hamilton, V. Dal Santo, R. Psaro, A. Caselli, *Green Chem.* **2014**, *16*, 3202.

Conjugated Organic Compounds for Solar Energy Conversion to Electricity and Fuels

Lorenzo Zani[a]

[a] *Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI); lorenzo.zani@iccom.cnr.it*

Over the years, conjugated organic compounds have been extensively employed in devices for solar energy exploitation, both as light-harvesting materials and semiconductors with high charge carrier mobility: relevant examples include sensitizers for dye-sensitized solar cells (DSSC) (1) and hydrogen photocatalytic production (2), small-molecule donor materials in organic solar cells (3) and hole-conductive materials for perovskite solar cells (4).
In this communication, we will provide an overview of our group's recent activity in the design, synthesis and application of donor-acceptor conjugated compounds for solar energy conversion (5-9). Compounds containing different heterocyclic rings (Figure 1) were assembled by means of typical organometallic and transition metal-catalyzed transformations, such as halogen-lithium exchange and Pd- or Cu-mediated coupling reactions, and were characterized using various spectroscopic and electrochemical techniques. The influence of their optical and redox properties on the efficiency of solar energy conversion devices will be discussed, together with the role of charge transfer processes taking place between them and other device components (such as inorganic semiconductors, electrolytes, sacrificial electron donors).

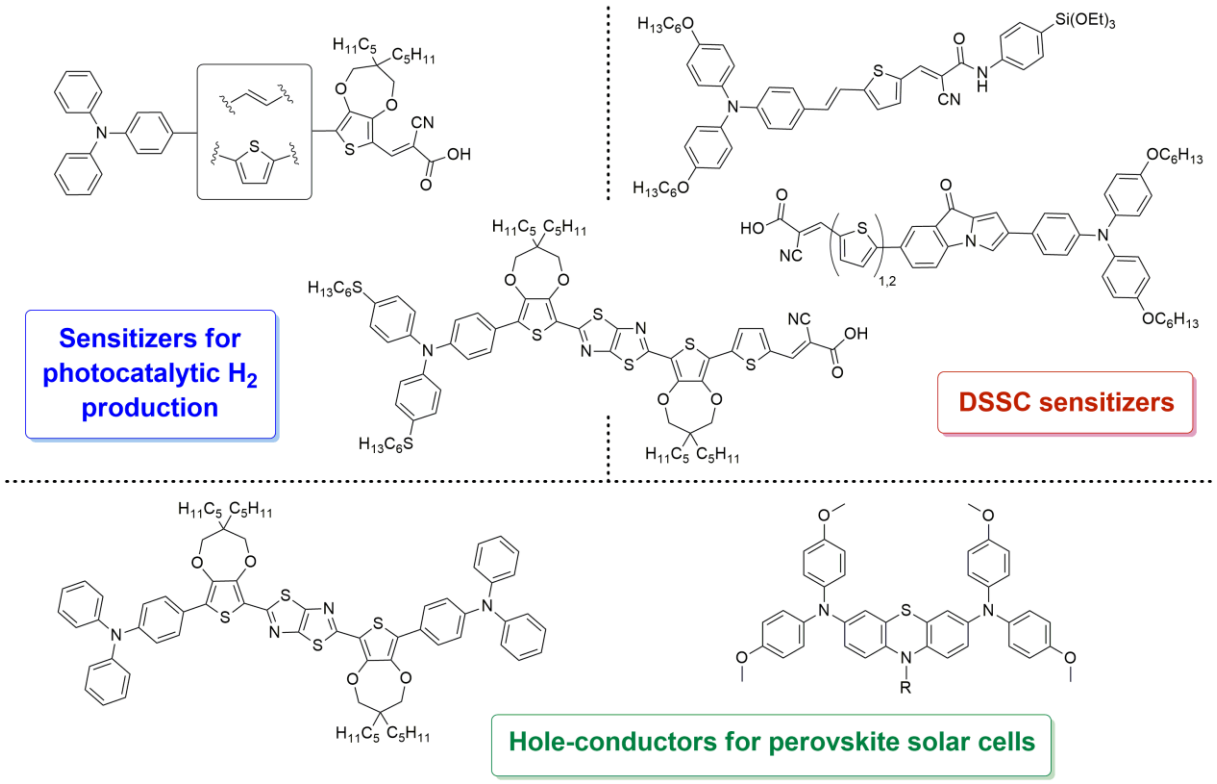


Figure 1. Examples of conjugated organic compounds employed in devices for solar energy exploitation.

References: 1. C.-P. Lee *et al.*, *RSC Adv.* **2015**, *5*, 23810. 2. B. Cecconi *et al.*, *Eur. J. Org. Chem.* **2016**, 5194. 3. A. Mishra, P. Bäuerle, *Angew. Chem. Int. Ed.* **2012**, *51*, 2020. 4. J. Seo *et al.*, *Acc. Chem. Res.* **2016**, *49*, 562. 5. A. Dessì *et al.*, *Chem. Commun.* **2014**, *50*, 13952. 6. D. Franchi *et al.*, *Tetrahedron* **2014**, *70*, 6285. 7. A. Dessì *et al.*, *RSC Adv.* **2015**, *5*, 32657. 8. B. Mátravölgyi *et al.*, *Eur. J. Org. Chem.* **2017**, 1843. 9. E. Castellucci *et al.*, *Phys. Chem. Chem. Phys.* **2017**, DOI: 10.1039/C7CP01956D.

Publishing your research in high impact journals

Andrew J. T. Shore[a]

[a] *Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, CAMBRIDGE, CB4 0WF, UK*

As Editor of *Dalton Transactions*, the Royal Society of Chemistry's flagship inorganic chemistry journal, I will present an overview on how to get your research published in high impact journals. I will also offer my personal hints and tips as an editor to guide you through the publication process and to be a successful published author. I will highlight the importance of publication ethics and the open access initiatives at the Royal Society of Chemistry.

Ab initio modeling of Metal-Organic Frameworks: from gas adsorption to stimuli responsive properties

BartolomeoCivalleri[a]

[a]*Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125 Torino (Italy)*

Metal-organic frameworks (MOFs) are amongst the most extensively studied hybrid framework materials and they have garnered major developments in the last decade mainly because of their nanoporous architectures and tunable physical and chemical properties (1). They are comprised of an inorganic part, usually formed by either metal ions or small clusters (e.g. metal-oxide) that acts as a node in a network, and an organic ligand that operates as a linker, or a spacer, among the nodes to form the framework through metal-ligand coordination bonds. In addition, they have a porous (and in most cases crystalline) structure that is architecturally stable with a high and ultra-high porosity. Traditionally, this has lead to applications such as gas storage and separation, catalysis and drug delivery (2).Nevertheless, the incredibly rich structural diversity and chemical versatility of such materials can lead to the emergence of many unique and novel properties that opens access to a wide spectrum of multifunctionalities not present in traditional materials (3). The exploration of structure-function relationships has then attracted considerable interests in broadening the combination of chemically bound organic and inorganic building blocks. Therefore, other promising technological applications have emerged, in particular, for electronics and opto-electronics, sensors and nonlinear optics (4).

Here, we give an overview of our recent results on a throughout theoretical characterization and prediction of adsorption properties of different MOFs from small to giant frameworks (5), structural flexibility and framework dynamics (6), as well as tunable electronic and dielectric properties in response to diverse physical and chemical stimuli (7).

The combined use of ab initio modeling in conjunction with experimental techniques (e.g. neutron and synchrotron spectroscopy or infrared and Raman spectroscopy) will be also highlighted.

All results have been obtained through a fully periodic ab-initio approach with the CRYSTAL program (8).

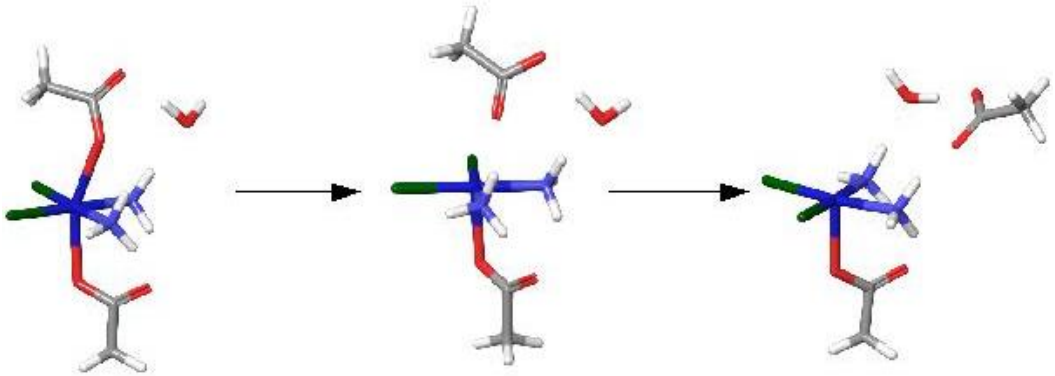
References: 1. H. Furukawa, K.E. Cordova, M. O'Keeffe, et al., Science 2013, 341, 1230444. 2. H.-C. Zhou, J.R. Long and O.M. Yaghi, Chem. Rev., 2012, 112, 673 3. M. D. Allendorf, V. Stavila, CrystEngComm, 2015,17, 229-246 4. V. Stavila, A. A. Talin, M. D. Allendorf, Chem. Soc. Rev. 2014, 43, 5994 5. L. Valenzano, B. Civalleri, K. Sillar, J. Sauer, J. Phys. Chem. C, 2011, 115, 21777. J. Ethiraj, E. Albanese, B. Civalleri et al. ChemSusChem, 2014, 7,3382.B. Civalleri, E. Albanese, M. D'Amore, R. Orlando, et al. in preparation. 6. M. R. Ryder, B. Civalleri et al., Phys. Rev. Lett. 113, 215502, 2014.M. R. Ryder, B. Civalleri, G. Cinque, et al., CrystEngComm 2016, 18, 4303. M. R. Ryder, B. Van de Voorde, B. Civalleri et al., Phys. Rev. Lett. 2017, in press. 7, A. M. Walker, B. Civalleri, B. Slater, et al., Angew.Chem. Int. Ed. 2010, 49, 7501. B. Civalleri, J.C. Tan, et al. in preparation 8.R. Dovesi, et al. Int. J. Quantum Chem. 2014, 114, 1287

Insight into the Electrochemical Reduction Mechanism of Pt(IV) Anticancer Complexes.

Iogann Tolbatov, Cecilia Coletti, Alessandro Marrone, Nazzareno Re

Università G. D'Annunzio Chieti-Pescara, Via dei Vestini 31, 66100 Chieti;nre@unich.it

A theoretical study was carried out on the mechanism of electrochemical reduction of the prototypical platinum(IV) anticancer complex $[Pt(NH_3)_2(CH_3COO)_2Cl_2]$ to the corresponding platinum(II) $[Pt(NH_3)_2(CH_3COO)_2]$ derivative.
Energies and geometric structures of the original Pt(IV) complex and all possible Pt(III) and Pt(II) intermediates and transition states during the reduction process have been calculated using several levels of theory, and allowed to formulate a detailed mechanism for the two-electron reduction of the $[Pt(NH_3)_2(CH_3COO)_2Cl_2]$ complex. Solvation was accounted for both by a continuum solvent model and through the inclusion of an increasing number of explicit water molecules.



The results show that, in agreement with the experimental evidence from cyclic voltammetry, the initial one electron reduction of the $[Pt^{IV}(NH_3)_2(CH_3COO)_2Cl_2]$ complex occurs through a stepwise mechanism via a metastable hexacoordinated platinum(III) $[Pt^{III}(NH_3)_2(CH_3COO)_2Cl_2]^-$ intermediate and a subsequent acetate ligand detachment with a low but significant activation free energy. On the other hand, the second electron reduction of the resulting pentacoordinated $[Pt^{III}(NH_3)_2(CH_3COO)Cl_2]$ species occurs through a barrierless concerted process to the final $[Pt^{II}(NH_3)_2(CH_3COO)_2]$ derivative. Accurate values for the redox potential were obtained in good agreement with the experimental data.
A deeper insight into the dependence of the mechanism of reduction of Pt(IV) complexes would be very important to understand its mechanism of action *in vivo* and may be useful to design new and more potent platinum(IV) anticancer drugs.

[1] Dhar, S.; Kolishetti, N.; Lippard, S. J.; Farokhzad, O. C. *Proc. Natl. Acad. Sci.* U.S.A. **2011**, 108, 1850.
[2] Meghan C. McCormick, Karlijn Keijzer, Abhigna Polavarapu, Franklin A. Schultz, and Mu-Hyun Baik, *J. Am. Chem. Soc.* **2014**, 136, 8992−9000.

Comunicazioni Orali

New methods and new catalysts for the oxygen reduction reaction at the cathode of fuel cells: surface science applied to CoO_x/Pd(100) ultrathin films

T. Kosmala, L. Calvillo, S. Agnoli, G. Granozzi

Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italia,
gaetano.granozzi@unipd.it

A great deal of efforts is currently taken for the development of innovative electroactive materials. A little travelled road envisages the use of ultrathin metal oxide films supported on metal substrate. As a matter of fact, these hybrid systems exhibit unprecedented structural and chemical properties and a wide gamut of special phenomena such as interfacial electronic hybridization and easy electron tunneling that can be exploited for a rational design of highly active catalysts. However, the subtle physics and chemistry ruling these systems require a sophisticated methodological approach for their study. With this aim, a rather unique home-lab set-up (see Fig.1), which allows combining X-ray photoelectron spectroscopy (XPS) and electrochemical measurements, has been used. We have prepared highly controlled CoO_x/Pd(100) model systems in UHV conditions (1), with atomic scale precision in order to study the activity of different prototypical cobalt oxide nanostructures (CoO and Co_3O_4 from nm to bulk dimension) and the influence of the Pd substrate on their chemical properties. Composition/structure/activity relationships have been established through a systematic study of their electrochemical behavior and the chemical/structural changes induced under working conditions. The combination of cobalt oxide with palladium allowed to obtain a very active material, with comparable activity with respect to pure palladium, but maintaining a higher poisoning tolerance due to the presence of the oxide. Moreover, thanks to the exploitation of an *in situ* technique we were able to identify the real active phase involved in ORR conditions. Such study demonstrates how the use of ultrathin hybrid films and *in situ* techniques can pave the way toward the development and comprehension of radically new electrodic materials.

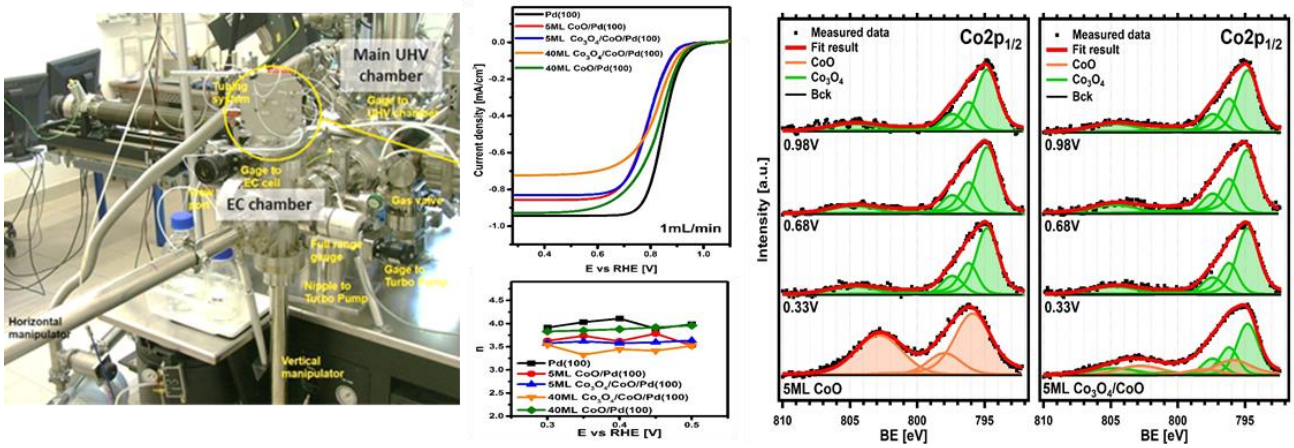


Figure 1: Experimental set-up for the in situ combined XPS and electrochemical measurements (left); LSV in O_2-saturated 0.1M KOH and number of transferred electrons for the CoOx/Pd(100) systems studied (middle); and Co $2p_{1/2}$ region for the CoO and Co_3O_4 systems at different potentials in O_2-saturated 0.1M KOH.

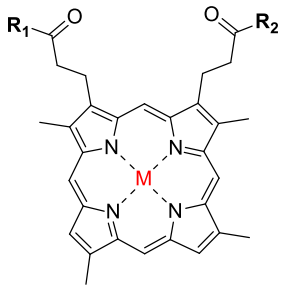
References:
1. L. Gragnaniello, S. Agnoli, G. Parteder, A. Barolo, F. Bondino, F. Allegretti, S. Surnev, G. Granozzi, F. P. Netzer, "Cobalt Oxide Nanolayers on Pd(100): The Thickness-Dependent Structural Evolution, *Surf. Sci.*, **604**, 2002–2011 (2010)

Control of enzymatic activity in a Mn-containing synthetic metalloenzyme

Daniele D'Alonzo[a], *Linda Leone*[a], *Marco Chino*[a], *Ornella Maglio*[a,b], *Flavia Nastri*[a], *Vincenzo Pavone*[c] *and Angela Lombardi*[a]

[a]*Department of Chemical Sciences, University "Federico II" of Napoli, Via Cintia 26, 80126, Napoli, Italy;* [b]*IBB-CNR, Via Mezzocannone 16, 80134, Napoli, Italy;* [c]*Department of Biology, University "Federico II" of Napoli, Via Cintia 26, 80126 Napoli (Italy); email: dandalonzo@unina.it*

Over the last decades, the search for cost-effective, highly efficient and chemically stable catalysts has inspired the development of synthetic metalloproteins. The aim is to reproduce the catalytic activity of natural enzymes while displaying a higher chemical stability (1). In this area, our interest is currently focused on the development of a new class of protein models, named *Mimochromes* (Figure 1). Mimochromes are composed of a deuteroporphyrin core, which is covalently linked to two peptide chains with a well-defined helical conformation, covering both planes of the heme and resulting in a helix-heme-helix sandwich structure. These enzymes are promising catalysts, exhibiting in many cases efficient peroxidase-like activity (2). To further expand the repertoire of artificial metalloenzymes with catalytic potential, we have herein studied the properties of the last-generation Mimochrome VIa, bearing Mn(III) as the metal ion. This was driven by the expected higher versatility of Mn-containing catalysts compared to the corresponding Fe(III) congeners, due to the higher number of accessible oxidation states (3).



M = Fe, [ref. 2]
M = Mn, **this work**

Mimochrome	R_1, R_2	
I	R_1=R_2	AcLAQL**H**ANKNH_2
II	R_1=R_2	AcDLSDL**H**SKKLKITLNH_2
IV	R_1=R_2	AcESQL**H**SNKRNH_2
III, V	R_1	AcDEHKL**H**SKKRKITLNH_2
	R_2	AcDEHKLYSKKRKITLNH_2
VI	R_1	AcDEQQL**H**SQKRKITLNH_2
	R_2	AcDEQQLSSQKRNH_2
VIa	R_1	AcDLQQL**H**SQKRKITLNH_2
	R_2	AcDEUQLSUQKRNH_2

H: Histidine coordinating the metal centre

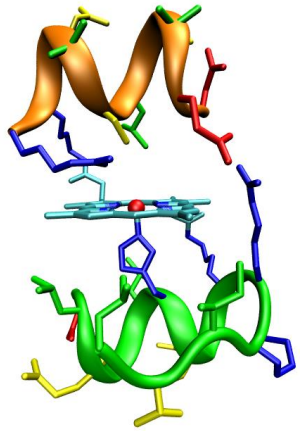


Figure 1. Fe- and Mn-containing protein models (Mimochromes).

Spectroscopic studies of the synthetic enzyme have enabled to detect a peculiar catalytic behavior, due to its ability to selectively work as a peroxidase (using an organic substrate as reducing agent) or as a catalase/dismutase (using the oxidizing agent as substrate). Interestingly, the control of the enzymatic activity is achieved by suitably varying the pH conditions. The analysis of the catalytic properties of the enzyme in model oxidation reactions has also been performed. In both cases, notable results have been obtained concerning both the conversion of the substrates and the selectivity of the transformations.

References:
1. Nastri, F.; Chino, M.; Maglio, O.; Bhagi-Damodaran, A.; Lu, Y.; Lombardi, A. *Chem. Soc. Rev.* **2016**, *45*, 5020-5054.
2. Vitale, R.; Lista, L.; Cerrone, C.; Caserta, G.; Chino, M.; Maglio, O.; Nastri, F.; Pavone, V.; Lombardi, A. *Org. Biomol. Chem.* **2015**, *13*, 4859-4868.
3. Carney, J. R.; Dillon, B. R.; Thomas, S. P. *Eur. J. Org. Chem.* **2016**, *23*, 3912-3929.

Effect of N-doping in the activity of TiO_2 supported catalysts in glycerol oxidation

CHERNI Dhia [a], MOUSSA Noomen [b], NCIB Mohammed Faouzi [c], PRATI Laura [d], VILLA Alberto [d]

[a] Faculty of sciences of Gabès, Erriadh city 6072 Zrig Tunisia; [b] National Engineering school of Gabès, Avenue Omar Ibn El Khattab 6072 Zrig Tunisia ; [c] Higher School of Sciences and Technology of Hammam sousse, Avenue Lamin Abbassi 4011 Tunisia; [d] Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano;
laura.prati@unimi.it

Glycerol constitutes an important renewable feedstock and its valorization greatly contributes to the economy of some processes mainly in the field of biofuels. Glycerol oxidation can produce a large amount of useful products and this research focuses on the effect of N-doping of the support (TiO_2) on the catalytic activity of AuPt catalysts in the selective glycerol oxidation for skipping the use of an external base. In fact, Au based catalysts have been shown to be active and selective in glycerol oxidation but it presents the drawback to be active only in the presence of an external base. It has been recently demonstrated that the addition of Pt allows the reaction to proceed under neutral conditions (1, 2) even the influence of the support is fundamental. In this work, we prepared N-doped TiO_2 via facile sol-gel method using different N-doping precursors during the synthesis [4-fluorobenzylamin (TNF), urea (TN) and chitosan (TNC)]. These materials were used for supporting preformed bimetallic AuPt nanoparticles. This preparation method allowed obtaining nanoparticles with comparable size and dispersion thus allowing studying the real influence of the support modification in the catalytic reaction.
All the catalysts appeared active in the selective oxidation of glycerol (Table 1) showing conversions in the range 53-92% after six hours of reaction with high selectivity to glyceric acid (74% -79%). Comparing the results using N-doped versus bare TiO_2 (entry 1, Table 1) we can conclude that the introduction of N-groups have a beneficial effect on the catalyst performance. Surprisingly, the most active catalyst is the one synthetized with chitosan, which presents the lowest N content. Most probably this results is correlated with the higher surface area observed in TiO_2 after the addition of chitosan.

Table 1. Glycerol oxidation in the presence of 1%wt AuPt/N-TiO_2

AuPt/TiO_2 +modifier	%at N [XPS]	%wt N [bulk]	Conv. (%)	Selectivity (%)				Mass balance (%)
				Tartronic Acid	Glyceric Acid	Glycolic Acid	dihydroxyacetone	
-	-	-	67.6	2.5	75.2	11.6	14.7	84.0
TN	0.6	46.5	78.4	2.3	77.7	10.4	11.1	97.9
TNF	0.6	11.2	73.4	2.4	74.9	11.7	13.6	93.6
TNC	0.0	8.7	92.1	2.6	79.9	17.2	11.8	79.5

Metal/Glycerol = 1/500; Glycerol = 0.3M; T° = 100°C; O_2 = 3atm; time = 6h

References:
1. A. Villa, G. M. Veith, L. Prati, Angew. Chem. 2010, 122, 4601–4604; Angew. Chem. Int. Ed. 2010, 49, 4499 – 4502.
2. G.L.Brett, Q.He, C.Hammond, P.J. Miedziak, N.Dimitratos, M.Sankar, A.A.Herzing, M.Conte, J.A.Lopez-Sanchez, C.J. Kiely, D.W. Knight, S.H.Taylor, G.J. Hutchings, Angew. Chem. 2011, 123, 10318 –10321.

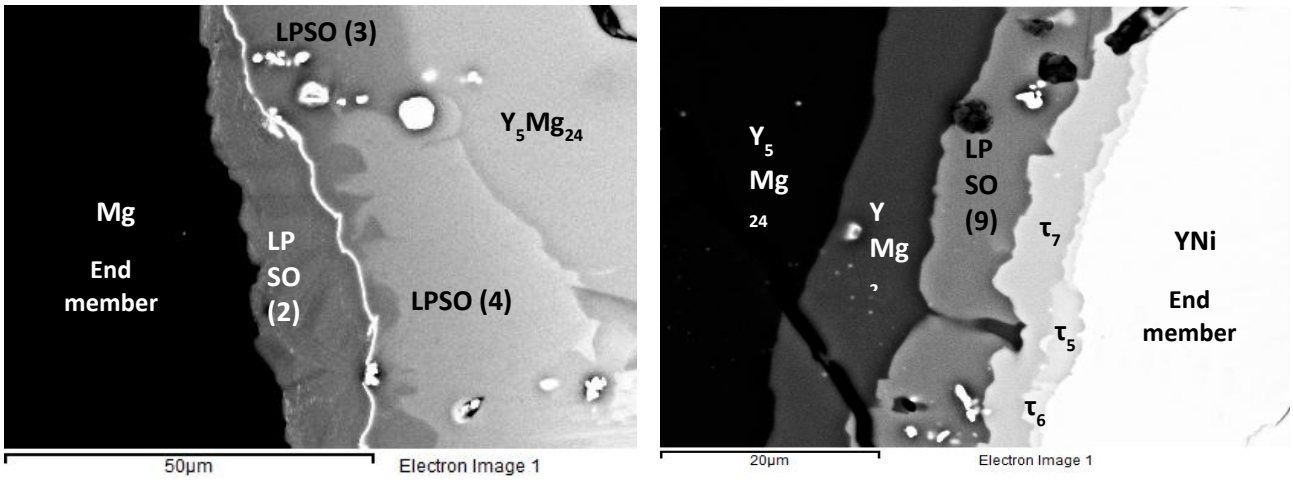
Long Period Stacking Ordered phases in the Y-Ni-Mg system: experimental and structural studies

Pavlo Solokha, Serena De Negri, Adriana Saccone

Dipartimento di Chimica e Chimica Industriale,Università degli Studi di Genova, Via Dodecaneso 31, 16146, Genova, Italy, e-mail: pavlo.solokha@unige.it

Long Period Stacking Ordered (LPSO) phases form a continuously growing family of compounds, whose peculiar structures are related to exceptional mechanical properties, such as high strength coupled with high ductility (1, 2). So far, LPSO phases were exclusively found in R-T-Mg (R = rare earth metal; T = transition element) systems and they are characterized by a magnesium content higher than 50 at.%; in fact, their crystal structures can be qualitatively described as composed of *hcp* Mg blocks of different thicknesses alternated with $R_xT_yMg_z$ slabs. Nevertheless, an accurate description of these phases is challenging, and complete structural models are rarely proposed. This is due both to their intrinsic structural complexity and to experimental problems related also to their mechanical properties (e.g. intricate microstructures, difficulties in single crystal selection and fine powder preparation).

In the framework of our studies on the constitutional properties of the Y-Ni-Mg system, numerous LPSO phases were detected, densely distributed along the 4:3 (Y:Ni) compositional line, the major part of which were not previously reported/described.



SEM image (BSE mode) of a diffusion couple Mg+YNi kept at 450 °C for 300 h (LPSO(2)-$Y_{7.2}Ni_{5.2}Mg_{87.6}$; LPSO(3)-$Y_{8.0}Ni_{6.2}Mg_{85.8}$; LPSO(4)-$Y_{9.8}Ni_{7.4}Mg_{82.8}$; LPSO(9)-$Y_{25.2}Ni_{19.3}Mg_{55.5}$; τ_5-$Y_{29.5}Ni_{26.9}Mg_{43.6}$; τ_6-$Y_4Ni_2Mg_3$; τ_7-YNiMg).

In this work, results on our studies on these compounds are presented, targeting different goals:

- Achievement of samples with more easily interpretable microstructures, in order to better distinguish between different, compositionally closed, LPSO phases and successively submit them to further analyses, such as transmission electron microscopy (TEM). For this purpose, diffusion couple experiments were designed and realized. Magnesium and Y-Ni binary alloys were chosen as end-members of the tested couples, which were successful to obtain well resolved layers of LPSO compounds (see figure).
- Generation of different structural models, to complement TEM-characterization results in order to fully describe the studied phases. For this purpose, an automated procedure is proposed, based on a joint application of the graph and group theories.

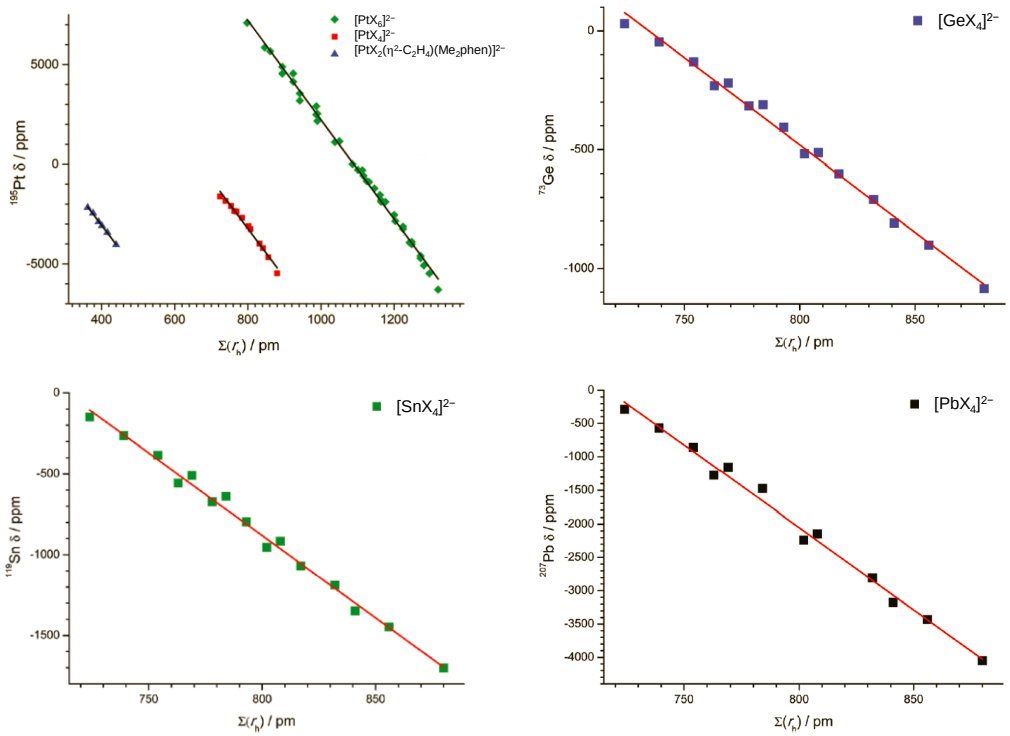
References: 1. F. Lu et al., *Rare metals* 31 (2012) 303. 2. D. Egusa, E. Abe, *Acta Mater.* 60 (2012) 166.

General cooperative effects of single atom ligands on the ^{73}Ge, ^{119}Sn and ^{207}Pb NMR signals of tetrahedral [MX_4] (M = Ge, Sn, Pb; X_4 = combination of Cl, Br, I) coordination compounds

Michele Benedetti[a], *Federica De Castro*[a], *Francesco Paolo Fanizzi*[a].

[a] *Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Monteroni, I-73100 Lecce, Italy. e-mail: michele.benedetti@unisalento.it*

The relation between atomic substituents, bonded to a central element, and the NMR chemical shift variations, observed on a central atom, is strongly debated. (1) We found that the ^{73}Ge, ^{119}Sn and ^{207}Pb NMR chemical shifts, and the halido ligands ionic radii overall sum, $\Sigma(r_h)$, are related by straight linear correlations in the tetrahedral [MX_4] (M = Ge, Sn, Pb; X_4 = combination of four Cl, Br, I) coordination compounds. This finding is well consistent with analogue linear relations, previously reported for series of octahedral, pentacoordinate, and square-planar Pt(II) and Pt(IV) complexes, see Figure. (2-4) Therefore, the analyzed ^{73}Ge, ^{119}Sn, and ^{207}Pb spectroscopic NMR data, confirm that even in [MX_4] tetrahedral complexes, the coordinated halido ligands could act on the central metal as shielding conducting rings. (5) Notwithstanding such general straight linear dependences found in the halide complexes of heavy metals {[MX_4], $[PtX_4]^{2-}$ and $[PtX_6]^{2-}$ (X_6 = combination of six F, Cl, Br and I), Ge(IV), Sn(IV), Pb(IV), Pt(II) and Pt(IV) heavy metal complexes} (1-5), as those here analyzed, many other halido derivatives seem to follow partially different behaviors. This suggests that the interactions defining the relations between the experimental NMR chemical shift of a central atom and the $\Sigma(r_h)$, need to be better understood. For this reason, a further work is in progress in order to clarify the factors, which are determining such altered correlations between experimental NMR chemical shifts of central atoms and the ionic radii overall sum of bonded halides, sometimes observed in [MX_n] derivatives.



References: 1. *Transition Metal Magnetic Resonance* (Ed.: P. S. Pregosin), Elsevier, Amsterdam **1991**; 2. M. Benedetti, P. Papadia, C. R. Girelli, F. De Castro, F. Capitelli, F. P. Fanizzi, *Inorg. Chim. Acta*, **2015**, *428*, 8-13; 3. M. Benedetti, F. De Castro, D. Antonucci, P. Papadia, F. P. Fanizzi, *Dalton Trans.*, **2015**, *44*, 15377-15381; 4. M. Benedetti, F. De Castro, F. P. Fanizzi, *Eur. J. Inorg. Chem.* **2016**, 3957-3962; 5. M. Benedetti, F. De Castro, F. P. Fanizzi, *Dalton Trans.*, **2017**, *46*, 2855-2860.

CO_2 capture by aqueous Na_2CO_3 combined with the formation of high quality $CaCO_3$ and the release of pure CO_2 at room conditions

Barzagli Francesco [a], *Giorgi Claudia* [b], *Mani Fabrizio* [a], *Peruzzini Maurizio* [a]

[a] *ICCOM CNR, via Madonna del Piano10, 50019 Sesto Fiorentino (FI), Italy;* [b] *University of Florence, Department of Chemistry, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; francesco.barzagli@iccom.cnr.it*

The reduction of anthropogenic CO_2 emissions is an urgent challenge, and strategies must be adopted to improve the efficiency of CO_2 capture and to reduce the costs of this technique.
As an alternative to traditional processes, in our laboratory has been developed a new concept of CO_2 capture technology which combines the CO_2 abatement with the production of commercially valuable products (1,2,3). This unconventional approach has the potential of circumventing the main drawbacks of the traditional processes of CO_2 capture (the energy penalties of absorbent regeneration, CO_2 compression and its disposal underground) by virtue of the formation of valuable commercial products.
Now we present the results of an alternative procedure of CO_2 capture by dilute aqueous solutions of Na_2CO_3 combined with the formation of high quality $CaCO_3$ and the release of pure CO_2 at room temperature and pressure.
$CaCO_3$ has an important market, estimated 74 million tonnes in 2011, and it is used in a wide range of applications in rubbers, paints, coatings, in cement industry and as a filler in the manufacture of paper and plastics.
The proposed process can be divided into two parts: i) the efficient CO_2 capture from a gas mixture by using the worldwide naturally available and cheap Na_2CO_3; ii) the production of $CaCO_3$ and the release of CO_2 at room temperature and pressure by reacting the CO_2 loaded solution with aqueous $CaCl_2$, an inexpensive by-product of the Solvay process and of potassium chlorate manufacture.
A continuous ^{13}C NMR spectroscopic investigation has enabled us to identify and quantify the species occurring in every step of the CO_2 capture process. The accurate study of the composition of CO_2 loaded solutions is crucial for the development of the more performing solutions in term of high efficiency of CO_2 capture and high degree of conversion into calcium carbonate.

References: 1. F. Mani, M. Peruzzini, P. Stoppioni. Energy Fuels, 2008, 22, 1714–1719. 2. F. Mani, M. Peruzzini, F. Barzagli. ChemSusChem, 2008, 1, 228-235. 3. F. Barzagli, F. Mani, M. Peruzzini. Journal of CO_2 Utilization, 2016, 13, 81-89.

Long-lived luminescent Quantum Dots as result of Reversible Electronic Energy Transfer

M. La Rosa [a], S. Silvi [b], G. Jonusauskas [c], N. D. McClenaghan [d], A. Credi [a]

[a] Dipartimento di Scienze e Tecnologie Agro-Alimentari, Università di Bologna Via Fanin 44, 40127 Bologna (Italia)

[b] Dipartimento di Chimica "G.Ciamician", Università di Bologna Via Selmi 2, 40126 Bologna (Italia),

[c] Laboratoire Ondes et Matière d'Aquitaine (LOMA), [d] Institut des Sciences Moléculaires (ISM), Université de Bordeaux/CNRS 351 Cours de la Libération, 33400 Talence (France),

marcello.larosa3@unibo.it

Electronic energy transfer is normally considered a unidirectional process from the donor to a suitable acceptor. However, if the excited states involved in such a process are sufficiently energetically close one to another, then the forward energy transfer can be followed by the back transfer from the acceptor to the donor, giving rise to the reversible electronic energy transfer (REET), and consequently establishing an equilibration between states. This process has been generalised in a range of molecule-based bichromophore systems, including molecular dyads (1) and non-covalent assemblies(2,3). However, to the best of our knowledge there is no example reported in literature concerning REET occurring in Quantum Dot (QD)-based (nano)systems. The QDs have the enormous advantage that their emitting state can be tuned by manipulating their size, thus providing a significant accuracy in projecting and developing of REET-based systems. Here we reported the first evidence of REET involving QDs and suitable chromophoric ligands attached to their surface. In our system the emitting state of a QD undergoes an equilibration with the long-lived triplet states of the chromophoric unit, thus resulting in the elongation of the lifetime of the QD by several orders of magnitude. Strong experimental evidence of such a process have been observed. Moreover, the effect of the oxygen, as well as of the size of the QDs have been also investigated.

References:
1. W. E. Ford, M. A. J. Rodgers. *J. Phys. Chem*. **1992**, *96*, 2917-2920.
2. L. Scarpantonio, A. Tron, C. Destribats, P. Godard, N. D. McClenaghan *Chem. Commun*. **2012**, *48*, 3981-3983.
3. S. A. Denisov, Q. Gan, X. Wang, L. Scarpantonio, Y. Ferrand, B. Kauffmann, G. Jonusauskas, I. Huc, N. D. McClenaghan *Angew. Chem*. **2016**, *128*, 1350-1355.

Grafene Functionalization and Tuning of Transport Properties by Plasma Strategies

G. V. Bianco[a], M. Grande[b], L. La Notte[c], E. Villari[c], M. M. Giangregorio[a], M. Losurdo[a], P. Capezzuto[a], A. Reale[c], A. D'Orazio[b], G. Bruno[a].

[a] *CNR-NANOTEC, Dipartimento di Chimica, Università degli Studi di Bari, 70126, Bari Italy;*
[b] *Dipartimento di Ingegneria Elettrica e dell'Informazione, Politecnico di Bari, Bari, 70126, Italy;*
[c] *CHOSE, Dipartimento di Ingegneria Elettronica, Università di Roma Tor Vergata, Roma,00133, Italy.*

The outstanding physical properties of graphene (ambipolar field effects, high room temperature mobility, optical transparency, etc) make this material promising for a number of applications in several fields (electronics, photonics, photovoltaics, etc.). Indeed, electrical, optical and chemical properties of graphene, which range from doping type, and surface wettability up to optical gap opening and modulation, should be carefully controlled and designed to satisfy specific requirements for practical device applications. To this aim, several theoretical and experimental works have investigated the chemical modifications of graphene as a mean for tuning the intrinsic material properties or for the introduction of new ones: opening of a band gap; improving wettability toward other materials of technological interest, providing selective interactions with analytes, etc.. Since graphene is characterized by a high chemical inertness, its functionalization typically involves the exploitation of free radicals addition reactions. Several strategies have been investigated for providing the generation of radical species in a controlled way including thermal, photochemical, and plasma processes. In particular, plasma chemistry offers a high potential in terms of process scalability but it often resulted in a low control of the functionalization processes as well as in the structural damaging of the materials.

In this contribution, we present mild modulated plasma processes for tailoring transport properties of large area chemical vapor deposition (CVD) graphene by functionalization with hydrogen (1), fluorine (2, 3) and oxygen species (4). The functionalization processes have been developed and optimized with the twofold aim: the fine control of graphene functionalization kinetics while minimizing the induced structural damage. This, together with the real time monitoring of graphene optical properties by spectroscopic ellipsometry, allows for an unprecedented control over the degree of functionalization.

The suitability of our functionalized graphene with engineered transport properties for applications in optics, optoelectronics and photovoltaics is experimentally demonstrated.

References:
1. G. Bruno, G. V. Bianco, et al, Phys.Chem.Chem.Phys., 2014, 16, 13948.
2. M. Grande, G. V. Bianco, et al, Scientific Reports, 2015, 5, 17083.
3. M. Grande, G. V. Bianco, et al, Optics Express, 2016, 24, 22788.
4. L. La Notte, G. V. Bianco, et al, Nanoscale, 2017, 9, 62.

Acknowledgements: The authors acknowledge the EU project TWINFUSYON (Horizon 2020, research and innovation programme under grant agreement No. 692034)

Drug delivery systems: hydrophilic gold nanoparticles for controlled drug loading and release

Iole Venditti[a], *M. Porchia*[b], *F. Tisato*[b], *C. Santini*[c], *M. Pellei*[c], *G. Iucci*[d], *C. Battocchio*[d], *C. Pietrosanti*[a], *G. Testa*[a], *I. Fratoddi*[a]

[a] *Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, 00187 Rome (IT);* [b]*ICMATE, National Research Council (CNR), Padua (IT);* [c] *Scuola di Scienze e Tecnologie–Sez. Chimica, Università di Camerino (IT);*[d] *Department of Science, ROMATRE University of Rome Viale Vasca navale 79Rome (IT); iole.venditti@uniroma1.it*

Drug delivery systems based on gold nanoparticles (AuNPs) are being widely applied, due to their unique chemical and physical properties, biocompatibility, and well-established strategies for surface modification.(1-4) In this framework we report studies about drug delivery systems based on gold nanoparticles stabilized by sodium 3-mercapto-1-propane sulfonate (Au-3MPS NPs) used as carrier for different drugs: the dexamethasone, DXM and copper complexes, Cu(I)R, based drugs. The drug loading and release were optimized for each delivery system and the bioconjugates were characterized by means of several technique, (Uv-visible, FTIR, XPS, DLS, FESEM, AFM). After optimization studies the best loading for Au-3MPS NPs @DXM have efficiency 80% , for Au-3MPS NPs @Cu(PTA)$_4$ have efficiency 78%. Studies regarding the release were performed in the range 1-14 days, showing at the end a drug release around 85% for each systems. The stability (see Fig.1) and citotoxicity studies on AuNPs confirm the biocompatibility of the drug delivery systems and open new exciting perspectives in the field in vitro and in vivo studies.(5,6)

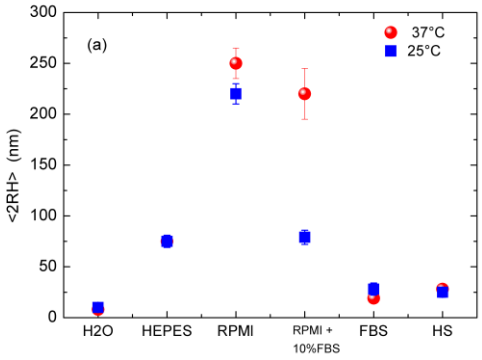


Fig.1. DLS data: <2R_H> show the stability of Au-3MPS NPs in different media (H_2O, HEPES, RPMI, complete RPMI, FBS, HS) and at different temperatures (25°C ■; 37°C ●)

References: 1. I. Fratoddi, et al., Nano Research 2015, 8, 1771. 2. I. Venditti, et al.; Colloids and Surfaces B: Biointerfaces 2015, 131, 93. 3. I. Venditti, et al., J. Colloid Interf. Sci., 2014, 418, 52. 4. C. Cametti et al., Langmuir 2011, 27, 7084. 5. V. Gandin, et al, J. Med. Chem. 2014, 57, 4745. 6. A. Rossi, et al., RCS Adv. 2016, 6, 99016.

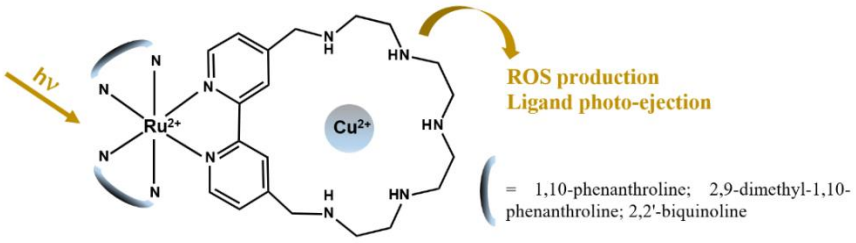
Novel strained ruthenium complexes in photodynamic therapy

Luca Conti, Andrea Bencini, Maria Giulia Fabbrini, Cristina Gellini, Claudia Giorgi, Giangaetano Pietraperzia, Barbara Valtancoli.

Department of Chemistry 'Ugo Shiff', University of Florence, Via della Lastruccia 3-50019-Sesto Fiorentino, Florence (FI), Italy
E-mail: luca.conti@unifi.it

Photodynamic therapy (PDT) is a field of growing interest in chemistry, which can be successfully employed in medicine for the treatment of a wide variety of skin diseases, bacterial infections and cancers. (1,2) It consists in the use of specific molecules (photosensitizer agents PS) which can be triggered by low energy light, leading to the production of active cytotoxic species (as reactive oxygen species ROS), which are in turn, able to bring serious damages to the biological environment, as DNA of cancer cells. (3) One of the main advantages of the PDT consists in the possibility to achieve a temporal and spatial control of the drug-activation, ensuring a discrimination between malignant and surrounding healthy tissues, and allowing to obtain a strong reduction of the dose-limiting side effects, commonly incurred with standard chemotherapies.

Many ruthenium polypyridyl complexes have been exploited in the PDT field since they have tunable absorption properties and induce $^1O_2$-mediated DNA photocleavage when exposed to visible light. However, in the case of hypoxic tumors, the reliance on molecular oxygen might preclude their application. For this reason it has been recently studied a new class of ruthenium polypyridyl complexes, characterized by the presence of a distortion feature in their octahedral geometry. The enhanced strain lowers the triplet metal-centered state (^{3}MC), allowing for thermal population from the triplet metal to ligand charge transfer state (^{3}MLCT), bringing to the loss of one or more ligands. (4) The resulting active species are then capable of forming covalent adducts with DNA, more difficult to repair respect on single strand breaks caused by $^1O_2$.



In this context we present a series of novel ruthenium (II) polypyridyl complexes (figure), containing 1,10-phenanthroline (phen) (L1) or 2,9-dimethyl-1,10'-phenanthroline (dmphen) (L2) or 2,2' biquinoline (biq) (L3) as ligands, and featuring the macrocycle 4,4'-(2,5,8,11,14-pentaaza[15])-2,2'-bipyridilophane (L'). From our studies emerges that these complexes are able both to produce oxygen singlet (L1) or release a ligand unit (L2, L3) upon photo-activation. In particular, L2 and L3 exhibit fast kinetics of the ligand photo-ejection processes, even by employing radiations within the therapeutic window. Furthermore, the introduction of the polyamine macrocycle L', able to strongly bind copper ion in physiological media, (5) makes possible to add the injury due to the Fenton reaction in the presence of a co-reactant (H_2O_2) to the damage provoked through photo-activation of such systems. These types of damage were evaluated towards pUC-19 plasmid by means of gel electrophoresis analysis.

Finally, investigations on the cytotoxic abilities of such potential drugs were performed towards selected cell lines.

References:
1. M. R. Hamblin, *Current Opinion in Microbiology*, **2016**, 33, 67–73
2. G. Boccalini, L. Conti, C. Montis, D. Bani, A. Bencini, D. Berti, C. Giorgi, A. Mengoni, B. Valtancoli, *J. Mater. Chem. B*, **2017**, 5, 2788-2797
3. J. M. M. Dąbrowski, L. G. Arnaut, Photochem. *Photobiol. Sci.*, **2015**, 14, 1765-1780
4. E. Wachter, D. K. Heidary, B. S. Howerton, S. Parking, E. C. Glazer, *Chem. Commun.*, **2012**, 48, 9649-9651.
5. F. Pina, A. Bencini, A. Bianchi, *Inorg. Chem.*, **2001**, 40, 2968-2975

Fluorescent solvatochromic molecules as probes for lipid bilayers

Simona Concilio[a], *Lucia Sessa*[b], *Antonio Massa*[c], *Stefano Piotto*[b], *Pio Iannelli*[b], *Rosita Diana*[d], *Barbara Panunzi*[d], *Ugo Caruso*[d].

[a] *Department of Industrial Engineering, University of Salerno;* [b] *Department of Pharmacy, University of Salerno;*
[c] *Department of Chemistry and Biology, University of Salerno;*
[d] *Department of Chemical Sciences, University of Napoli "Federico II"*
sconcilio@unisa.it

In recent years, the study of cell membranes has been the subject of a great interest in biological research. Lipid bilayers are made up of numerous phospholipids, which, according to their structure, charge, and interaction with membrane proteins and cytoskeletal proteins, spontaneously organize in aggregates having different fluidity (e.g. liquid ordered, L_o and liquid disordered, L_d). Among the techniques for membrane characterization, fluorescence microscopy is the most common used and one of the less invasive for the cell (1). The red edge excitation shift (REES) of a fluorophore depends on the slow solvent reorientation around a fluorophore in the excited state. REES can be used to monitor the environment and dynamics around it in an organized molecular assembly (2,3). Different fluorescent probes, with a different charge, polarity, and magnitude, have been developed containing lipid chains of various lengths (4). In spite of the large number of available probes, it often remains the problem of membrane perturbation, which the probe itself causes when inserted.
The aim of this work is the design and the synthesis of new fluorescent solvatochromic probes containing a fluorophore and characterized by an inverted phospholipid structure, able to interact with the heads of the phospholipids of a membrane and not fully internalized in the lipid bilayer (Fig. 1).

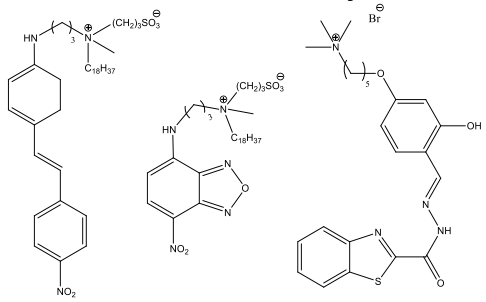


Figure 1 – chemical structure of some of the synthesized probes

In particular, NBD group possesses some of the most desirable solvatochromic properties to serve as an excellent probe for both spectroscopic and microscopic applications, since fluorescence lifetime of the NBD group exhibits sensitivity to environmental polarity (5). The fluorescence behavior of these probes has been characterized both in organic solvents and in model membranes. Computational methods have been used to evaluate the metal binding and the interaction of probes with model membranes.

References: **1.** Baumgart, T.; Hunt, G.; Farkas, E.R.; Webb, W.W.; Feigenson, G.W. Fluorescence probe partitioning between l o/l d phases in lipid membranes. *Biochimica et Biophysica Acta (BBA)-Biomembranes* **2007**, *1768*, 2182-2194. **2.** Reichardt, C. Solvatochromic dyes as solvent polarity indicators. *Chemical Reviews* **1994**, *94*, 2319-2358. **3.** Kachel, K.; Asuncion-Punzalan, E.; London, E. The location of fluorescence probes with charged groups in model membranes. *Biochimica et Biophysica Acta (BBA)-Biomembranes* **1998**, *1374*, 63-76. **4.** Klymchenko, A.S.; Kreder, R. Fluorescent probes for lipid rafts: From model membranes to living cells. *Chemistry & biology* **2014**, *21*, 97-113. **5.** Sasaki, H.; White, S.H. A novel fluorescent probe that senses the physical state of lipid bilayers. *Biophysical journal* **2009**, *96*, 4631-4641.

Platinum(II) complexes of ligands containing OH functional groups: synthesis, reactivity and antiproliferative properties

Simona Samaritani[a], *Daniela Belli Dell' Amico*[a], *Marialuigia Colalillo*[a], *Luca Labella*[a], *Fabio Marchetti*[a], *Mariafrancesca Hyeraci*[b], *Aída Nelly García-Argáez*[b], *Lisa Dalla Via*[b]

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy;* [b] *Dipartimento di Scienze del Farmaco, Università degli Studi di Padova, Via F. Marzolo 5, 35131 Padova, Italy*

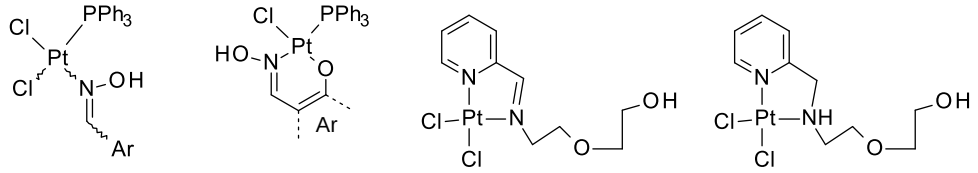
simona.samaritani@unipi.it

Following the discovery of the anticancer properties of cisplatin(1), hundreds of new platinum(II) complexes are prepared and tested every year. Although different mechanisms of action can be involved, it is generally accepted that the main target of these bioactive molecules is DNA. The platination of DNA generally involves the coordination of purine bases to activated, hydrolyzed forms of the metal complexes and can be greatly helped by additional interactions such as hydrogen bonding. As a matter of fact, good results have been described for some platinum complexes characterized by the presence of OH groups on coordinated ligands(2). Indeed, among the non-conventional, *trans* triphenylphosphino complexes $[PtCl_2(PPh_3)(R_2NH)]$ recently prepared by us(3), promising *in vitro* data were observed for R = CH_2CH_2OH(3e).

In this contribution we report:

i) the preparation and the characterization of Pt(II) complexes containing, besides PPh_3, a monodentate and/or bidentate arylaldoxime ligand (complexes a and b, respectively) and

ii) the synthesis of pyridinimino (c) and pyridinamino (d) complexes, bearing a terminal hydroxyl group.



(a) (b) (c) (d)

Complexes a and b are reactive under basic conditions, due to the enhanced acidity of OH oxime group upon complexation to the metal, allowing the preparation of some rare dinuclear derivatives as well as the functionalization of OH oxime group. Complexes b were tested *in vitro* against some human cancer cell lines and preliminary data show an interesting antiproliferative activity (IC_{50} ~ 1-10 μM).

Complexes c and d show enhanced affinity towards water and are good candidates as antiproliferative agents. Moreover, their further functionalization is possible, exploiting the known reactivity of hydroxyl group.

References:

1. B. Rosenberg, L. Van Camp, T. Crigas Nature 205 (1965) 698.
2. a) Y. Y. Scaffidi-Domianello, A. A. Legin, M. A. Jakupec, A. Roller, V. Y. Kukushkin, M. Galanski, B. K. Keppler, Inorg. Chem. 51 (2012) 7153; b) Y. Y. Scaffidi-Domianello, K. Meelich, M. A. Jakupec, V. B. Arion, V. Y. Kukushkin, M. Galanski, B. K. Keppler, Inorg. Chem. 49 (2010) 5669; c) A. G. Quiroga, L. Cubo, E. de Blas, P. Aller, C. Navarro-Ranninger, J. Inorg. Biochem. 101 (2007) 104; d) F.J. Ramos-Lima, O. Vrána, A.G. Quiroga, C. Navarro-Ranninger, A. Halámiková, H. Rybníćková, L. Hejmalová, V. Brabec, J. Med. Chem. 49 (2006) 2640.
3. a) D. Belli Dell' Amico, L. Bellucci, L. Labella, F. Marchetti, S. Samaritani, Polyhedron 119 (2016) 403; b) D. Belli Dell' Amico, L. Labella, F. Marchetti, S. Samaritani, G. A. Hernández-Fuentes, A. N. García-Argáez, L. Dalla Via, Polyhedron 119 (2016) 396; c) L. Dalla Via, A. N. García-Argáez, E. Agostinelli, D. Belli Dell'Amico, L. Labella, S. Samaritani, Bioorg. Med. Chem. 24 (2016) 2929;d) D. Belli Dell' Amico, L. Dalla Via, A. N. García-Argáez, L. Labella, F. Marchetti, S. Samaritani, Polyhedron 85 (2015) 685; e) L. Dalla Via, A. N. García-Argáez, A. Adami, S. Grancara, P. Martinis, A. Toninello, D. Belli Dell'Amico, L. Labella, S. Samaritani, Bioorg. Med. Chem. 21 (2013) 6965.

Killing bacteria via ion-complexing polymeric materials

Lorella Izzo[a], *Margherita De Rosa*[a], *Giovanni Vigliotta*[a], *Annunziata Soriente*[a], *Vito Capaccio*[a], *Giuliana Gorrasi*[b], *Renata Adami*[b], *Ernesto Reverchon*[b], *Massimo Mella*[c]

[a] *Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II, 132 – 84084- Fisciano (SA);* [b] *Dipartimento di Ingegneria Industriale, Università degli Studi di Salerno, Via Giovanni Paolo II, 132 – 84084- Fisciano (SA);* [c] *Dipartimento di Scienza ed Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio, 11 – 22100 Como; E-mail lizzo@unisa.it*

New copolymers containing either MMA and 18C6 crown ether pedants, or PEG, MMA, and 18C6 crown ether pedants were synthesized via uncontrolled radical polymerization or ATRP to test the idea that sequestering structural alkali-earth ions from bacterial Outer Membrane (OM) may lead to bacterial death. ATRP allowed to produce Y-like architecture to investigate structural effects already evidenced for copolymers containing DMAEMA rather than 18C6 pedants (1,2). It was found that copolymer plaques were able to complex Mg(II)/Ca(II) ions and also showed antimicrobial activity when placed in pure water *E. coli* suspensions, albeit with different efficiencies (Figure 1).

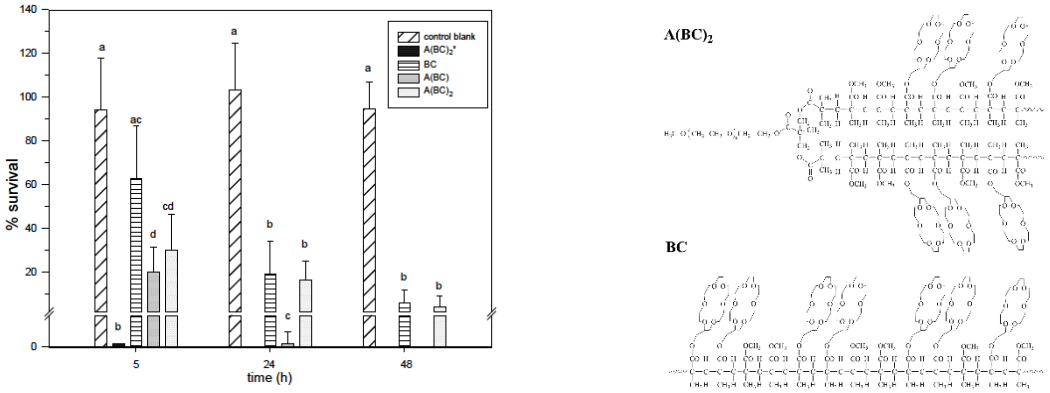


Figure 1. E. coli % survival vs time for 18C6-containing polymers. $A(BC)_2^*$ is a copolymer containing DMAEMA instead of 18C6, and linear mPEG-b-PMMA copolymer is used as the control.

Different plaque porosities and surface morphology, as evidenced by both TGA-determined water adsorption and direct visualization with FE-SEM, were considered as responsible for the differences in antimicrobial efficiency.

The role of the 18C6 was elucidated by pre-saturating plaques with Mg/Ca ions obtaining a marked reduction in antimicrobial efficiency in the first 5 h of contact with bacteria.

The latter finding indicated that the plaque complexation ability is a key ingredient in bacterial killing at short contact time (< 5h). At longer times, the mode of action is instead related to the polycationic nature acquired by the plaque due to ions sequestering.(3)

References:

1. G. Vigliotta, M. Mella, D. Rega, L. Izzo *Biomacromolecules* **2012**, *13*, 833-841
2. S. Matrella, C. Vitiello, M. Mella, G. Vigliotta, L. Izzo *Macromol. Biosci*. **2015**, *15*, 927–940.
3. M. De Rosa, G. Vigliotta, A. Soriente, V. Capaccio, G. Gorrasi, R. Adami, E. Reverchon, M. Mella, L. Izzo *Biomat. Sci*. **2017**, *5*, 741-751.

Novel gold(I) and silver(I) metal complexes as promising antibacterial candidates

Damiano Cirri[a], *Tiziano Marzo*[b], *Alessandro Pratesi*[a], *Luigi Messori*[a]

[a]*Laboratory of Metals in Medicine (MetMed), Department of Chemistry "U. Schiff", University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy;* [b]*Department of Chemistry and Industrial Chemistry (DCCI), University of Pisa, Via Moruzzi, 13, 56124 Pisa, Italy; damiano.cirri@unifi.it*

Several metals and metal-based compounds have been used for centuries as anti-infective agents on a simple empirical basis, with some appreciable result. For instance, the complex dicyanoaurate(I) was proposed and used by Koch as an antitubercular agent in the pioneering times of modern pharmacology, while several bismuth, antimony and mercury compounds have been extensively employed to fight various bacterial and parasitic diseases.(1-4) Yet, more recently, due to the advent of the golden era of antibiotics and to grounded concerns on their conspicuous systemic toxicity, metal-based agents were gradually abandoned. However, during the last two decades, the so called "antibiotic resistance crisis", arising from the emergence of bacterial strains with multidrug-resistant (MDR) and extensively drug-resistant (XDR) phenotypes, and from the simultaneous decline in the discovery rate of new and effective antibiotic molecules, has posed the dramatic problem of finding out new substances capable of fighting life-threatening infections caused by these pathogens.(5,6) Metal-based compounds were thus reconsidered as a rich source of antimicrobial agents often endowed with innovative modes of action. In this context auranofin (AF), an antiarthritic agent still sporadically used to treat some severe forms of rheumatoid arthritis, has been extensively revisited within new drug repurposing strategies with promising results. Indeed, remarkable antimicrobial and antiparasitic properties were disclosed for this oral gold(I) drug, that has become the reference compound even for the development and the studies of novel gold-based antibacterial agents or specific inhibitors of important enzymes.(6,7) Yet, the precise mechanisms of the antimicrobial action of AF and the respective biomolecular targets are not known. The promising antibacterial properties detected for AF prompted us to expand this kind of investigations even further, working not only with AF but also with a series of silver(I) and gold(I) analogues with general structure Et_3PMX that were recently prepared in our laboratory. Comparative analysis of the results allowed us to define some remarkable structure activity relationships in this series of linear metal complexes as detailed below:

1. The thiosugar ligand is not essential for the antimicrobial activity of AF.
2. The nature of the X group in the Et_3PAuX series is not relevant for the activity.
3. Altogether, the above results point to the $[AuPEt_3]^+$ moiety as the true pharmacophore in this series of metal complexes; their antimicrobial activity probably arises from gold coordination to appropriate targets upon ligand exchange.
4. Unexpectedly, replacement of gold with silver causes a net reduction in activity. Thus the presence of the gold(I) center is a major determinant of the antimicrobial properties.

Overall, we have shown here that selective modifications of the Auranofin scaffold may be conveniently exploited to modulate the antimicrobial profiles; important insight is gained into structure-activity relationships inherent to this class of metal compounds. The comparative analysis of the respective antimicrobial profiles is a valid tool to select the "best performers" to be further evaluated as innovative and more efficient antimicrobial metal-based drugs. Hints are obtained to design better metal based antimicrobial agents.

References: 1. Benedek, T.G. *J. Hist. Med. Allied Sci.*, 2004, **59**, 50-89. 2. Shaw III, C.F. *Chem. Rev.*, 1999, **99**, 2589-2600. 3. Singh, S.; Sivakumar, R. *J. Infect. Chemother.*, 2004, **10**, 307-315. 4. Lemire, J.A.; Harrison, J.J.; Turner, R.J. *Nat. Rev. Microbiol.*, 2013, **11**, 371-384. 5. Ventola, C.L. *P&T*, 2015, **40**, 277-283. 6. Cassetta, M.I.; Marzo, T.; Fallani, S.; Novelli, A.; and Messori, L. *Biometals*, 2014, **27**, 787. 7. Hikisz, P.; Szczupak, Ł.; Koceva-Chyła, A.; Gu Spiel, A.; Oehninger, L.; Ott I.; Therrien, B.; Solecka, J.; Kowalski, K. *Molecules*. 2015, **20**, 19699-19718.

The inorganic side of neurotrophins: metal coordination and new therapeutic perspectives

Diego La Mendola[a], Giuseppe Pandini[b], Cristina Satriano[c], Adriana Pietropaolo[d], Irina Naletova[c], Fiorenza Gianì[b], Alessio Travalia[e], Vincenzo G. Nicoletti[f], Giuseppe Arena[c], Enrico Rizzarelli[c]

[a] Dipartimento di Farmacia, Università di Pisa, Via Bonanno Pisano 6, 56126, Pisa (Italy); [b] Dipartimento di Clinica e medicina sperimintale, Endocrinologia Ospedale Garibaldi, Università di Catania, via Palermo n. 636, 95122 Catania (Italy), Italy; [c] Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania (Italy); [d] Dipartimento di Scienze della Salute, Università di Catanzaro, Viale Europa, 88100 Catanzaro (Italy; [e] Centre for Neural Science, New York University, 4 Washington Place, New York, NY, USA; [f] Dipartimento di Scienze Biomediche e Biotecnologiche, Università di Catania,

E-mail: lamendola@farm.unipi.it

Neurotrophins (NTs) are secreted proteins essential for development, maintenance and survival of central and peripheral nervous systems. The main NTs are the nerve growth factor (NGF) and the brain derived neurotrophic factor (BDNF), which play an essential role in neuroplasticity, memory, learning in the adult nervous system and their impairment may be involved in several degenerative disorders, including Alzheimer's Disease (AD). According to the metal hypothesis some d-block metal ions play a crucial role in AD, and neurotrophins performs their activity in the same brain areas affected by metal dyshomeostasis in pathological conditions. Thus, it is conceivable that transition metal ions could play selective physiological/pathological roles by modulating NTs activity. High concentrations of Zn^{2+} and Cu^{2+} have been shown to modulate the *in vitro* effects of NGF and BDNF. Taking into account the essential role played by NTs in the presence of metal ions, they have been considered for the treatment of neurodegenerative diseases, to induce spinal cord repair and neurogenesis. A promising strategy to overcome current limits in their effective therapeutic application (such as poor plasma stability, side effects due to concomitant binding to multiple receptor, pain, poor penetration in the blood brain barrier (BBB) involves the use of peptides retaining the most essential elements of neurotrophic action. The N-terminal region of NGF and BDNF as well as of other NTs is critical for the binding selectivity and activation of their specific Trk receptors.
We studied the Cu^{2+} and Zn^{2+} complexes with neurotrophins' N-terminal domain by means of potentiometric and spectroscopic (UV/Vis, CD, NMR and EPR) techniques and DFT calculations. The coordination features of single point mutated peptides were also characterized to better define the metal coordination environment and the involvement of the N-terminal amino group in metal binding. Metal binding to these peptides modulate their proliferative activity similarly to that observed with the whole protein. The peptide NGF(1-14) partly exerts an effective and specific NGF-like action on some crucial NGF intracellular targets such as cAMP-response element binding protein (CREB), able to induce dendritic spine growth, morphology change, synaptic plasticity, and long-term memory.(1) Finally, live cell imaging experiments of PC12 treatment with fluorescent labelled peptide NGF(1-14)FAM, show that the peptide is able to pass cellular membrane and acts as a ionophore, increasing the intracellular amount of copper.

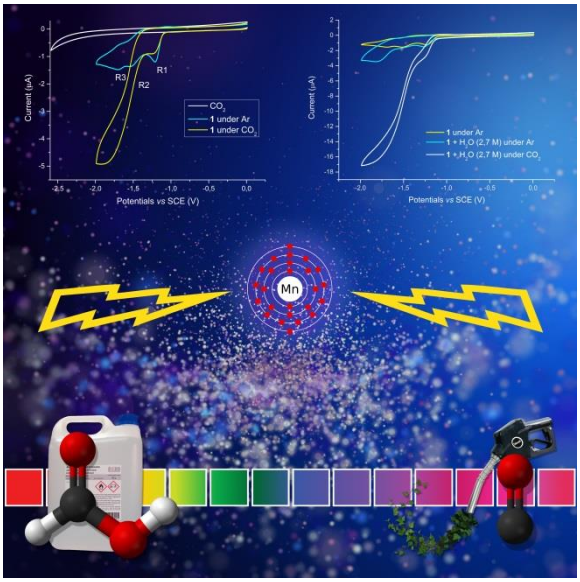
References: 1. G. Pandini, C. Satriano, A. Pietropaolo, F. Gianì, A. Travaglia, D. La Mendola, V.G. Nicoletti, E. Rizzarelli, Front. Neurosci. (2016) 10, 569.

Homogenous and Heterogeneous Transition Metal Catalysts for CO_2 Reduction

Roberto Gobetto, Carlo Nervi

Dept. of Chemistry. University of Torino, Via P. Giuria n° 7, 10125 Torino, Italy; roberto.gobetto@unito.it

The catalytic conversion of the extremely stable CO_2 molecule to usable fuels or chemical products is a critical goal that would positively impact the global environment, hopefully helping in overcoming some of the problems of energy crisis.(1) Valuable products, such as carbon monoxide, formic acid and high molecular-weight polymers, obtained from the electrochemical conversion of CO_2, have been indicated as chemicals that can store intermittent energy source like the solar light, thus balancing power supply, energy demand and environmental concerns of greenhouse gas emissions. A possible approach to reduce the large overpotentials required for this multi-electron process is the use of organometal molecular compounds, able to catalyze CO_2 reduction through proton-assisted processes.(2,3) In this presentation an overview of our recent advances in the use of organometallic complexes as catalysts for electrochemical CO_2 reduction will be illustrated. Enhanced catalytic activity and clear mechanistic pathway will be discussed. Analogies and differences among several transition metal complexes will be outlined, including the better known mechanism based on Re(bpy) complexes, the effect of local proton sources on the Mn(bpy) complexes [4] as well as some outline on the use of earth-abundant transition metal complexes (Mo and W) [5] employed as redox catalysts for CO_2 electrochemical reduction.



Relatively few studies were focused on the heterogeneous electrochemical catalysis despite the large number of potential advantages such as easier recovery of products and catalysts, small amounts of catalyst necessary for efficient electrolysis, deactivation pathways often hindered or suppressed and elimination of solubility problems. Furthermore, in a heterogeneous system the electron transfer will be more efficient to the attached or bonded catalyst compared with that in solution, lowering the limitation of the electron transfer in the catalytic cycle. Transition metal complexes immobilized on electrode surfaces can represent promising catalysts to be utilized in a large-scale process for CO_2 reduction, particularly if non-precious metals like cobalt, iron, nickel, copper, and zinc are involved. We very recently exploited the electropolymerization properties of Re(bpy) complexes containing the thiophene moiety that have the advantage to produce an electron-conducting film, with interesting results.(6,7)

References: 1. J. Ronge, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordiga and J. A. Martens, *Chem. Soc. Rev.* **2014**, *43*, 7963–7981. 2. C. Costentin, M. Robert and J.-M. Saveant, *Chem. Soc. Rev.* **2013**, *42*, 2423–2436. 3. F. Franco,; C. Cometto,; F. Ferrero Vallana,; F. Sordello,; C. Minero,; E. Priola,; C. Nervi,; R. Gobetto, *Chem. Commun.* **2014**, *50*, 14670-14673. 4. F. Franco, C. Cometto, L. Nencini, C. Barolo, F. Sordello, C. Minero, J. Fiedler, M. Robert, R. Gobetto, C. Nervi, *Chem. Eur. J.* **2017**, *23*, 4782-4793. 5. F. Franco, C. Cometto, F. Sordello, C. Minero, L. Nencini, J. Fiedler, R. Gobetto, C. Nervi, *ChemElectroChem* **2015**, *2*, 1372-1379. 6. C. Sun, S. Prosperini, P. Quagliotto, G. Viscardi, S. S. Yoon, R. Gobetto and C. Nervi, *Dalton Trans.* **2016**, *40*, 5656-5661. 7. C. Sun, R. Gobetto, C. Nervi, *New J. Chem.* **2016**, *40*, 5656-5661.

A new series of Ag and Au carbene complexes with interesting anticancer properties

Mariconda A.[a], Longo P.[a], Saturnino C.[b], Lemba R.[b], Sinicropi M.S.[c]

[a]Department of Chemistry & Biology, University of Salerno, 84084 Fisciano, Italy; [b]Department of Pharmacy, University of Salerno, 84084 Fisciano, Italy; [c]Department of Pharmacy,Health & Nutritional Sciences, University of Calabria, 87036 Arcavacata di Rende, Italy.
E-mail: amariconda@unisa.it

Elemental silver and its salts have long been known for their antimicrobial properties, predominantly against chronic ulcers, extensive burns and wounds.(1) Gold and its complexes like aurothiomalate, aurothiosulfate or auranofin were recognized to be effective drugs for the treatment of rheumatoid arthritis. The research on potential utilization in medicinal chemistry of new complexes of both metals has experienced a renaissance over the last decades.(2) Silver (I) and gold (I) N-heterocyclic carbene (NHC) complexes have emerged as a new generation of potential anticancer agents due to their high cytotoxicity and stability. Metal N-heterocyclic carbene complexes readily fit the requirements for an efficient drug design and fast optimization.(3)
Recently, we have reported the synthesis and the anticancer properties of three new silver and three new gold NHCs complexes, having a methyl group and an alkyl ß-hydroxy derivative as *N,N'*-substituents (Fig. 1). The most active antitumor compounds were holding a lipophilic structure and they did not affect the proliferation of nontumorigenic epithelial breast cells.(4)
In the literature, 4,5-dichloro-1H-imidazole complexes (5,6) are promising molecules with antibacterial and anti-tumor activity.
Thus, we have synthesized and tested anticancer activity of two carbene complexes of silver and gold, derived from 4,5-dichloro-1H-imidazole having a methyl group and an alkyl ß-hydroxy derivative as *N,N'*-substituents and in order to increase the lipophilicity of these compounds, we have synthesized also the complexes having in the position 4,5 of the imidazole ring two phenyl groups (Fig. 2). The complexes were characterized by NMR and mass-spectroscopy and by elemental analysis. The biologic action of these complexes was tested in vitro against two cancer cell lines MCF-7 and Hela, showing an interesting antiproliferative activity.

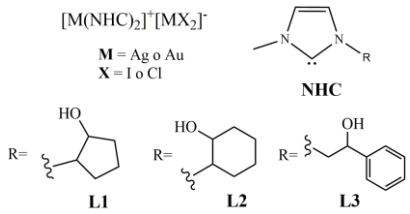


Fig. 1 Silver and gold NHCs complexes

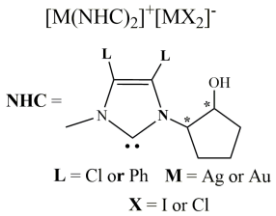


Fig. 2 New silver and gold NHCs complexes

References: 1. S. Budagumpi, R.A. Haque, S. Endud, G. Ur Rehman, A.W. Salman Eur. J. Inorg. Chem. 2013, 25, 4367–4388. 2. R. Rubbiania, E. Schuhb, A. Meyera, J. Lemkec, J. Wimbergd, N. Metzler-Noltec, F. Meyerd, F. Mohrb, I. Otta Med Chem Comm 2013, 4, 942-948. 3. C.Q. Hu, X. Li, W. Wang, R.Y. Zhang, L.P. Deng Curr. Med. Chem. 2014, 21, 1220–1230. 4. C. Saturnino, I. Barone, D. Iacopetta, A. Mariconda, M.S. Sinicropi, C. Rosano, A. Campana, S. Catalano, P. Longo, S. Ando Future Medicinal Chemistry 2016, 8, 2213-2229. 5. T.J. Siciliano, M.C. Deblock, K.M. Hindi, S. Durmus, M.J. Panzner, C.A. Tessier, W.J. Youngs J. Organomet. Chem. 2011, 696, 1066–1071. 6. D.A. Medvetz, K.M. Hindi, M.J. Panzner, A.J. Ditto, Y.H. Yun, W.J. Youngs, Metal-Based Drugs 2008, 2008, 384010.

NMR studies on copper transport proteins interacting with silver nanoparticles

Maria I. Nardella[a], *Vincenzo Mangini*[b], *Antonio Rosato*[a], *Fabio Arnesano*[a], *Giovanni Natile*[a]

[a] *Department of Chemistry, University of Bari, via E. Orabona, 4, 70125 Bari, Italy;* [b] *Center for Biomolecular Nanotechnologies@UniLe, Istituto Italiano di Tecnologia (IIT) via Barsati 73010 Arnesano, Lecce, Italy*

E-mail: maria.nardella@uniba.it

Despite the widespread use of silver nanoparticles, little is known about the potential risks arising from the silver nanoparticles (AgNPs) themselves and from the silver ions released from them. Since Ag(I) or Cu(I) have similar coordination properties, an impact on copper metabolism is expected. Cells utilize several pathways to ensure uptake, storage and export of copper. In humans, the Cu chaperone Atox1 delivers Cu(I) to the metal-binding domains (MBDs) of two P1B-type ATPases: the Menkes (Atp7a) and Wilson (Atp7b) disease proteins.[1;2] Both Atox1 and the first MBD of Menkes (Mnk1) bind one Cu(I) through two Cys residues located in a conserved CXXC motif.[3] Thus, the aim of our work has been to gain direct evidence by NMR of the interaction of Atox1 and Mnk1 with Ag(I) or AgNPs. Although the two proteins have quite similar structure, their behaviors is substantially different.

AgNPs are also characterized by a remarkable antibacterial effect, thus monitoring the interactions of AgNPs with bacterial cells can be crucial for elucidating the origin of the bactericidal activity and for expanding their biomedical and environmental applications. Therefore, we have investigated the Ag metabolism in gram-negative bacteria, by a forefront technique called in-cell NMR.[4] E. coli cells overexpressing Atox1 were treated with Ag salts. In-cell NMR revealed that, within treated cells, Atox1 undergoes only minor changes. In contrast, after the lysis of the cells, the protein appears to be bound to the metal. From these data, it can be inferred that the scarce reactivity of Atox1 with Ag(I) inside the cell can be due to compartmentalization (e.g. in the periplasm) and/or sequestration of the metal ion. Further studies are ongoing to trace the fate of Ag(I) ions within E. coli cells and to unravel the mechanisms used by gram-negative bacteria to become resistant to xenobiotics. This latter is a particularly hot issue, especially after the recent discovery of an E. coli strain resistant to the last-resort antibiotic Colistin.[5]

Acknowledgment

This work was supported by the Italian “Ministero dell’Università e della Ricerca” (FIRB 2011-RINAME, RBAP114AMK). We gratefully acknowledge “Anna Laura Segre” fellowship for support to V.M. We also thank the University of Bari and the Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici (C.I.R.C.M.S.B.).

References:

1. I. H. Hung, R. L. Casareno, G. Labesse, F. S. Mathews, J. D. Gitlin, J.Biol.Chem. 1998, 273 1749-1754.
2. S. Lutsenko, K. Petrukhin, M. J. Cooper, C. T. Gilliam, J. H. Kaplan, J.Biol.Chem. 1997, 272 18939-18944.
3. F. Arnesano, L. Banci, I. Bertini, S. Ciofi-Baffoni, E. Molteni, D. L. Huffman, T. V. O'Halloran, Genome Res. 2002, 12 255-271.
4. H. Li, H. Sun, Metallomics. 2014, 6 69-76.
5. N. Stoesser, A. J. Mathers, C. E. Moore, N. P. Day, D. W. Crook, Lancet Infect.Dis. 2016, 16 285-286.

New Differently Sized Neutral and OctacationicPorphyrazines. Physicochemical Properties and Potentialities as Anticancer Drugs.

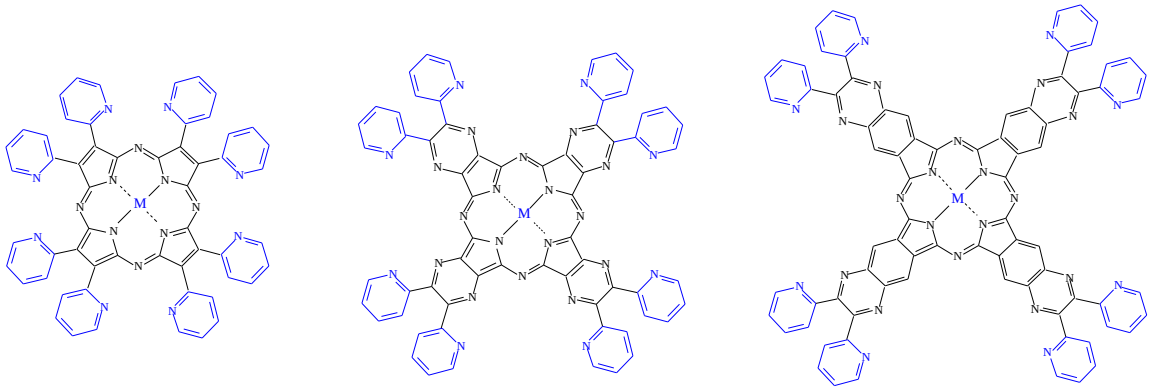
Maria Pia Donzello[a], *Elisa Viola*[a], *Claudio Ercolani*[a]

[a] *Dipartimento di Chimica, Università di Roma Sapienza, P.le Aldo Moro, 5 - 00185 Roma, Italy*

As part of our recent studies on porphyrazine compounds, UV-visible solution studies in DMF proved that a progressive extension of the central tetrapyrrolic π-eletron delocalized system for the triad of externally octapyridinated Mg^{II} porphyrazine complexes [$Py_8PzMg(H_2O)$], [$Py_8TPyzPzMg(H_2O)$], and [$Py_8QxPzMg(H_2O)$] (Scheme 1; M = $Mg^{II}(H_2O)$), sensibly moves the Q-band maximum toward the red; the observed spectral changes were adequately interpreted by DFT/TDDFT calculations (1).

The spectroscopic and electrochemical properties of the newly synthesized smaller macrocycles, ie. the unmetalated species [Py_8PzH_2] and the metal derivatives [Py_8PzM] with M = Co^{II}, Cu^{II}, Zn^{II}, and Mg^{II} included, were also examined and the data compared with those of the related more expanded macrocycles [$Py_8TPyzPzM$] (Scheme 1B) and [Py_8QxPzM] (Scheme 1C). The photosensitizer activity for the generation of singlet oxygen, $^1O_2$, was explored for the neutral species [Py_8PzM] (M = $Mg^{II}(H_2O)$, Zn^{II}) in DMF, with found Φ_Δ values 0.42 and 0.64, respectively (2).

The related water soluble octacations $[(2\text{-Mepy})_8PzM]^{8+}$ (M = $Mg^{II}(H_2O)$, Zn^{II}), carrying externally N-methylated 2-pyridyl rings, isolated as iodide salts, are present in H_2O/SDS solution exclusively in their monomeric form. Both species exhibit Φ_Δ values 2.3-2.5 higher than the value measured for the standard $PcAlS_{mix}$, a vey promising response in view of their potential application as anticancer drugs in photodynamic therapy (PDT). Studies on the differently sized Zn^{II} octacations $[(2\text{-Mepy})_8PzZn]^{8+}$, $[(2\text{-Mepy})_8TPyzPzZn]^{8+}$ and $[(2\text{-Mepy})_8QxPzZn]^{8+}$ as to their possible interaction with a G-quadruplex structure and ds DNA are in due course (3).



A: [Py_8PzM] B: [$Py_8TPyzPzM$] C: [Py_8QxPzM]

Scheme 1

References: 1. Donzello, M. P.; De Mori, G.; Viola, E.; Ercolani, C.; Ricciardi, G.; Rosa, A. *Inorg. Chem*. **2014**, 53, 8009. 2. Sciscione, F.; Cong, L.; Donzello, M. P.; Viola, E.; Ercolani, C.; Kadish, K. M. *Inorg. Chem*. **2017**, *56*, 5813. 3. Sciscione, F.; Manoli, F.; Viola, E.; Wankar, J.; Ercolani, C.; Donzello, M. P.; Manet, I. manuscript in preparation.

Auranofin, Et_3PAuCl and Et_3PAuI exert high *in vitro* cytotoxic effects toward colorectal cancer cell lines: a comparative chemical, biological and mechanistic study

Tiziano Marzo[a,b], Damiano Cirri[b], Chiara Gabbiani[a], Alessandro Pratesi[b], Tania Gamberi[c], Francesca Magherini[c], Annalisa Guerri[b], Tarita Biver[a], Annarosa Arcangeli[d] and Luigi Messori[a]

[a] Department of Chemistry and Industrial Chemistry (DCCI), University of Pisa, Via Moruzzi, 13, 56124 Pisa, Italy; [b] Laboratory of Metals in Medicine (MetMed), Department of Chemistry "U. Schiff", University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy; [c] Department of Biochemical, Experimental and Clinical Sciences "Mario Serio", University of Florence, Viale GB Morgagni 50, 50134, Firenze, Italy; [d] Department of Experimental and Clinical Medicine, University of Florence, Viale GB Morgagni 50, 50134 Firenze, Italy.

tiziano.marzo@dcci.unipi.it

Auranofin [2,3,4,6-tetra-o-acetyl-L-thio-β-D-glyco-pyrano-sato-S-(triethyl- phosphine)-gold(I)] (AF) is a clinically established oral chrysotherapeutic agent that is used for the treatment of some severe forms of rheumatoid arthritis (1). During the last few years, this drug, has attracted renewed attention in the medicinal chemistry scientific community as a prospective anticancer and antimicrobial agent according to innovative drug repurposing strategies (2-4). In particular, AF has been, or still is, the object of clinical trials in the US as an anticancer agent (5,6). We thought that selective and limited chemical modifications of AF might lead to a modulation and hopefully an improvement of its pharmacological profile. The solution behavior of Et_3PAuI, Et_3PAuCl and Auranofin, as well as their interactions with a hen egg white lysozyme and a standard single strand oligonucleotide, were comparatively analyzed through NMR spectroscopy and ESI-MS. Binding ability of the three complexes toward ds-DNA was also assessed by ethidium bromide displacement and viscometric tests. The cytotoxic effects toward two representative colorectal cancer cell lines were found to be strong and similar in the three cases and a good correlation could be established between the cytotoxicity and the ability to inhibit thioredoxin reductase. Remarkably, no cytotoxic effect was found on normal cell lines. Overall, a very similar profile emerges for Et_3PAuI and Et_3PAuCl, that retain the potent cytotoxic effects of Auranofin, while showing some peculiar features. These results demonstrate that the presence of the thiosugar moiety is not mandatory for the pharmacological action, suggesting that the tuning of some relevant chemical properties such as lipophilicity could be exploited to improve bioavailability, with no loss of the pharmacological effects.

References:
1. Shaw, III C.F. *Chem. Rev.*, **1999**, *99*, 2589-2600.
2. Cassetta, M.I.; Marzo, T.; Fallani, S.; Novelli, A.; Messori, L. *Biometals*, **2014**, *27*, 787-791.
3. Fiskus, W.; Saba, N.; Shen, M.; Ghias, M.; Liu, J.; Gupta, S.D.; Chauhan, L.; Rao, R.; Gunewardena, S.; Schorno, K.; Austin, C.P.; Maddocks, K.; Byrd, J.; Melnick, A.; Huang, P.; Wiestner, A.; Bhalla, K.N. *Cancer Res.*, **2014**, *74*, 2520-2532.
4. Madeira, J.M.; Gibson, D.L.; Kean, W.F.; Klegeris, A. *Inflammopharmacology*, **2012**, *20*, 297-306.
5. Phase I and II Study of Auranofin in Chronic Lymphocytic Leukemia (CLL), to be found under https://clinicaltrials.gov/ct2/show/NCT01419691.
6. Auranofin in Treating Patients With Recurrent Epithelial Ovarian, Primary Peritoneal, or Fallopian Tube Cancer, to be found under https://clinicaltrials.gov/ct2/show/NCT01747798.

Acknowledgements: This work was funded by AIRC-FIRC through IG-16049 (PI: Prof. L. Messori) and 3-years Fellowship for Italy (PI: Dr. T. Marzo, Project Code: 18044), Beneficentia Stiftung (Vaduz).

Hydrogen Evolution Catalyzed by Cobalt Mimochrome VIa

Vincenzo Firpo[a], *Gerardo Zambrano*[a], *Vincenzo Pavone*[b], *Kara L. Bren*[c] *and Angela Lombardi*[a]

[a] *Department of Chemical Sciences, University ''Federico II'' of Naples, Via Cintia 26, 80126, Naples, Italy;*
[b]*Department of Biology, University of Naples "Federico II'', Via Cintia 26, 80126, Naples, Italy;*
[c]*Department of Chemistry, University of Rochester, Rochester, New York, USA; email: vincenzo.firpo@unina.it*

Molecular hydrogen is an energy-dense fuel that has collected significant interest as alternative to fossil fuels (1). In order to be sustainable, hydrogen must be produced from water electrolysis utilizing carbon free energy and using catalysts based on earth-abundant elements (2). Natural hydrogenases evolve H_2 from neutral water with high efficiency and activity, but oxygen sensitivity of many hydrogenases and their difficulty to be handled render them unsuitable candidates for industrial applications (3). Nowadays there is an increasing demand in developing molecular functional hydrogenase mimics, as they are more amenable to detailed manipulation and study. Cobalt-porphyrin-containing biomolecular catalysts have shown their capability in reducing proton to molecular hydrogen in neutral water (4), therefore, they represent valid noble-metal free catalysts for such reaction. For example, cobalt-microperoxidase 11, a cobalt-porphyrin-peptide complex, is an efficient catalyst for hydrogen evolution from neutral water in the presence of oxygen (4). Stimulated by these findings, we have studied Cobalt-Mimochrome VIa (CoMC6a) as a robust and water soluble catalyst for hydrogen evolution. CoMC6a comprises the deuteroporphyrin core, covalently linked to two peptide chains in helical conformation, covering both porphyrin faces. It presents a helix-porphyrin-helix sandwich structure and a penta-coordinated metal site (Figure 1).

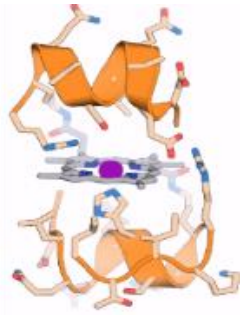


Figure 1. Molecular model of Cobalt Mimochrome VIa

CoMC6a shows hydrogenase activity in water solution at neutral pH under aerobic conditions. It works as molecular electrocatalyst for hydrogen evolution with near quantitative Faradaic efficiency, an overpotential value of 850mV, a TOF of $4.7s^{-1}$. Remarkably, CoMC6a exhibits a TON of $3x10^5$, which is one order of magnitude higher compared to the other cobalt porphyrins (4). These results suggest that the "sandwich" structure surrounding the porphyrin moiety may play a protective role from bleaching.

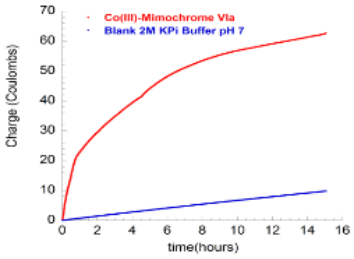


Figure 2. 16h controlled

CoMC6a is an interesting model that can help us to understand the structural requirements needed to enhance hydrogen evolution reactions. In this context, our future efforts will be aimed at modifying the peptide scaffold, to develop novel enzymes with lower overpotential values, and, consequently, more competitive respect to the currently catalysts.

References:

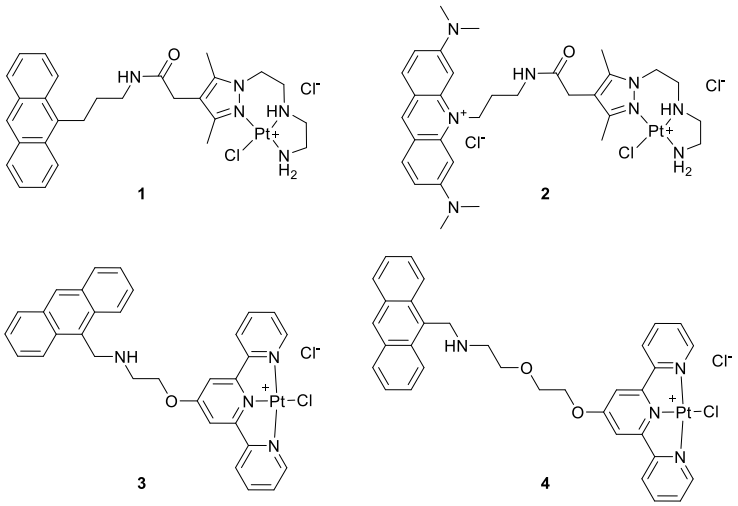
1 Schultz, M. G.; Diehl, T.; Brasseur, G. P.; Zittel, W. *Science* **2003**, *302*, 624.
2. Cook, T. R.; Dogutan, D. K.; Reece, S. Y.; Surendranath, Y.; Teets, T. S.; Nocera, D. G. *Chem. Rev*. **2010**, *110*, 6474.
3. Fontecilla-Camps, J. C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. *Chem. Rev*. **2007**, *107*, 4273.
4. Kleingardner, J. G.; Kandemir, B; Bren, L. B. *J. Am. Chem. Soc*. **2014**, *136*, 4.
5. Nastri, F.; Lista, L.; Ringhieri, P.; Vitale, R.; Faiella, M.; Andreozzi, C.; Travascio, P.; Maglio, O.; Lombardi, A.; Pavone, V.; *Chem. Eur. J.* **2011**, *17*, 4444.

Bifunctional triamine Pt(II) complexes containing a DNA intercalating moiety

Elisabetta Gabano[a], *Sofia Gama*[b], *Ramon Vilar*[c], *Mauro Ravera*[a], *Domenico Osella*[a]

[a] *Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale T. Michel 11, 15121 Alessandria, Italy;* [b] *Centro de Ciências e Tecnologias Nucleares (C²TN), Instituto Superior Técnico, Universidade de Lisboa, Portugal;* [c] *Department of Chemistry, Imperial College London, London SW7 2AZ, UK; elisabetta.gabano@uniupo.it*

Different strategies can be exploited to improve the activity of Pt-based antitumor drugs and the design of bifunctional drugs is one of the most intriguing one since synergistic effects of the two parts are expected. In particular, in this work alkylating Pt(II) complexes have been combined to DNA intercalators. Monochlorido Pt(II) complexes with tridentate pyrazolyl-diamine ligands are able to form only monofunctional adducts with DNA, being generally less active than cisplatin. However, the incorporation into such Pt complexes of a functional group, able to interact with or intercalate into DNA, such as anthracene or acridine orange (**1** and **2**), increased their activity (1,2).



The *in vitro* evaluation of these complexes comprised: *i)* cytotoxicity against ovarian carcinoma A2780 and A2780cisR cell lines; *ii)* interaction with supercoiled DNA; *iii)* cellular and nuclear uptake. The anthracenyl-containing complex **1** displayed a covalent type of binding with DNA, whereas the acridine orange counterpart **2** showed a combination of intercalative and covalent binding modes with a strong contribution from the former. Complex **1** showed a very strong antiproliferative activity on cell lines A2780 and A2780cisR and both **1** and **2** were able to significantly overcome cisplatin cross-resistance. The encouraging results on the antitumor activity of Pt(II) complexes **1** and **2** led to an extension of the study to related Pt(II) complexes with anthracenyl-containing terpyridine ligands (**3** and **4**). These derivatives showed affinity for quadruple-stranded DNA (G-quadruplex) with a good selectivity over duplex DNA, whereas the free ligands did not have significant affinity for any DNA sequences, indicating that the presence of the metal is essential for high affinity and selectivity. Moreover, the presence of a longer linker between the Pt core and the anthracene moiety enhances the interaction with G-quadruplex (3).

References:
1. C. Francisco, S. Gama, F. Mendes, F. Marques, I. C. Santos, A. Paulo, I. Santos, J. Coimbra, E. Gabano, M. Ravera, Dalton Trans., 40 (2011) 5781–5792.
2. S. Gama, F. Mendes, T. Esteves, F. Marques, A. Matos, J. Rino, J. Coimbra, M. Ravera, E. Gabano, I. Santos, A. Paulo, ChemBioChem, 13 (2012) 2352 -2362.
3. S. Gama, I. Rodrigues, F. Mendes, I. C. Santos, E. Gabano, B. Klejevskaja, J. Gonzalez-Garcia, M. Ravera, R. Vilar, A. Paulo, J. Inorg. Biochem., 160 (2016) 275–286.

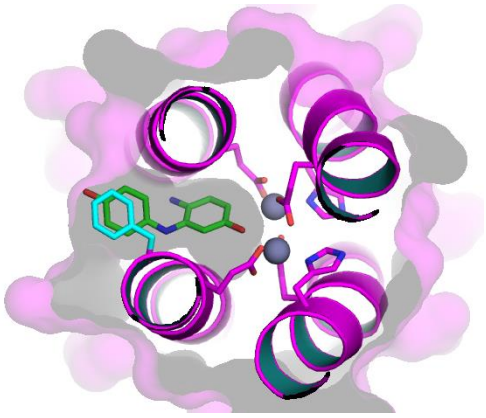
Minimizing the release of reactive intermediates in O_2-dependent oxidation by *de novo* metalloenzymes

Linda Leone[a], *Marco Chino*[a], *Ornella Maglio*[b], *Vincenzo Pavone*[c], *Flavia Nastri*[a], *Angela Lombardi*[a]

[a]*Department of Chemical Sciences, University of Napoli "Federico II" - Via Cintia 26, 80126 Napoli (Italy);* [b]*Institute of Biostructures and Bioimages-IBB, National Research Council, Via Mezzocannone 16, 80134 Napoli (Italy);* [c]*Department ofBiology University of Napoli "Federico II, Via Cintia 26, 80126 Napoli (Italy)"; linda.leone@unina.it*

Dioxygen activation and its transformations are key reactions both in chemistry and biology. In biological systems,these reactions are often catalyzed by transition metal cofactors.The desire to develop catalysts that match or even exceed the performance of natural enzymes has stimulated researchers towards the construction of functional metal sites into peptide/protein-based architectures by protein design (1,2,3,4). Successful examples of *de novo* designed oxygen-activating metalloproteins are the DF (*Due Ferro*) proteins, which fold into a four-helix-bundle structure. These catalysts oxidize quinols to corresponding quinones (5,6) upon O_2 reduction, while cycling between di-Fe(II) and di-Fe(III) states.

One of the key questions in protein design is to understand how different protein environments influence the properties of the bound cofactor or substrate. Starting from the DF protein scaffold, we used a recently developed design protocol (7) for constructing a heterodimeric four-helix bundle by covalent ligation of two α_2 chains through click chemistry. By modulating the substrate interactions within the active site, we designed an artificial metalloenzyme, DF-Click1, that catalyzes a net four-electron O_2 reduction in two consecutive two-electron steps inside the protein. Differently from earlier DFs, DF-Click1 catalyzes the oxidation of 4-amino-phenol (4AP) without releasing H_2O_2 or other reactive species. This catalyst further promotes an oxidative coupling between one molecule of oxidized and reduced 4AP at the active site. The diiron site of DF-Click1 is able to perform O_2-dependent phenol-oxidase activity preventing the reactive intermediates from diffusing in solution, filling a gap between *de novo* designed and natural proteins.



Docking model of 4AP dimer into the active site of DF-Click1.

References:

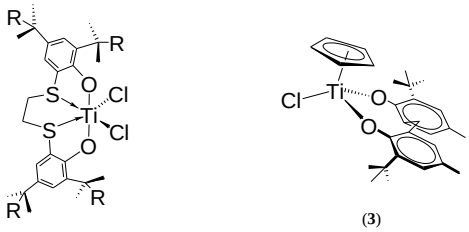
1. F. Nastri, M. Chino, O. Maglio, A. Bhagi-Damodaran, Y. Lu, Angela Lombardi *Chem. Soc. Rev.* 1-35 (2016).
2. M.V. Doble, A.C.C. Ward, P.J. Deuss, A.G. Jarvis and P.C.J. Kamer *Bioorg.Med. Chem.* 22, 5657–5677(2014).
3. F. Nastri, R. Bruni, O. Maglio, A. Lombardi *Coordination Chemistry in Protein Cages*, ed. T. Ueno, Y. Watanabe, John Wiley & Sons, Hoboken, New Jersey, pp. 45–85 (2013).
4. F. Yu, V.M. Cangelosi, M.L. Zastrow, M. Tegoni, J.S. Plegaria, A.G. Tebo, C.S. Mocny, L. Ruckthong, H. Qayyumand V.L. Pecoraro *Chem. Rev*., *114*, 3495-3578 (2014).
5. R. Torres Martin de Rosales, M. Faiella, E. Farquhar, L. Que Jr, C. Andreozzi, V. Pavone, O. Maglio, F. Nastri, A. Lombardi *Biol. Inorg. Chem.* 15, 717–728 (2010).
6. R.A. Snyder, J. Betzu, S.E. Butch, A.J. Reig, E.I. Solomon, W.F. DeGrado *Biochemistry* 54, 4637−4651 (2015).
7. M. Chino, L. Leone, O. Maglio, A. Lombardi *Methods Enzymol.* 580, 471-499 (2016).

Biosourced Polymers from Stereoregular Polymerization of Monoterpenes in the Presence of Homogeneous Titanium Catalysts.

Carmine Capacchione, Marco Naddeo, Ermanno Luciano, Antonio Buonerba, Alfonso Grassi and Antonio Proto

Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano

The shift from conventional, fossil chemical feedstock to renewable resources is one of the main objectives of the chemical industry in recent decades. In this context many efforts have been devoted to synthesis of polymers by renewable resources. In particular carbohydrates, fatty acid and lignin have been intensively studied as possible starting materials. (1) Conversely, in spite of their widespread presence in natural products such as essential oils, terpenes have received little attention as viable candidate for the synthesis of polymers from biomasses. Regardless of their structural diversity they can be viewed as hydrocarbons consisting of the repetition of isoprene units (C_5). The acyclic simplest monoterpenes (C_{10}) due to their structural features can give rise to a chemistry very close to that of 1,3 alkadienes deriving from fossil sources . In particular β-myrcene obtained in large scale from turpetine, has showed to be an excellent starting material for the synthesis of a wide range of useful chemicals.(2)



(**1**) R = CH_3
(**2**) R = Ph

(**3**)

Figure 7. Titanium[OSSO]-type (**1**-**2**) and titanium monocyclopentadienyl (**3**)complexes.

More recently the stereoregular polymerization of β-myrcene and its isomer β-ocymene has been reported to be promoted by catalysts based on lanthanides.(3) Among the possible microstructures both the 1,4-trans-polymyrcene and 1,4-cis-polymyrcene have been obtained. Cui and coworkers also reported the isoselective synthesis of 3,4-polymyrcene in the presence of a lutetium bearing a NSN-type ligand. (4)

Titanium is the second most abundant transition metal on the earth-crust, therefore the development of catalytic systems based on this metal is advantageous from both the environmental and economical points of view. It is worth noting that notwithstanding the central role played by titanium in polymerization catalysis there are no examples to date of titanium based catalysts able to efficiently promote the polymerization of these monoterpenes to stereoregular polymers.

In this contribution we report on the synthesis of stereoregular polymers of β-myrcene and β-ocymene and their copolymers with styrene by using the homogeneous titanium catalysts the [OSSO]-type complexes **1** and **2** and monocyclopentadienyl Ti(η^5-C_5H_5)-(κ^2-MBMP)Cl (**3**) (MBMP = 2,2'-methylenebis(6-*tert*-butyl-4-methylphenoxo) complex that have already shown to be active and versatile catalysts, when activated by methylaluminoxane (MAO), for the stereoregular polymerization of various 1,3-alkadienes and their copolymerization with styrene.(5)

References: 1. Llevot, A.; Dannecker, P.-K.; von Czapiewski, M.; Over, L. C.; Söyler, Z.; Meier, M. A. R. *Chem. Eur. J.* **2016**, *22*, 11510 – 11521. 2. Behr, A.; Johnen, L.; *ChemSusChem*, **2009**, *2*, 1072-1095. 3. Georges, S.; Toure, A. O.; Visseaux, M.; Zinck, P. *Macromolecules* **2014**, *47*, 4538-4547. 4. Liu, B.; Li, L.; Sun, G.; Liu D.; Li, S.; Cui, D. *Chem. Commun*. **2015**, *51*, 1039-1041. 5. Buonerba, A. Fienga, M.; Milione, S.; Cuomo, C.; Grassi, A.; Proto, A. Capacchione, C. *Macromolecules* **2013**, *46*, 8449-8457.

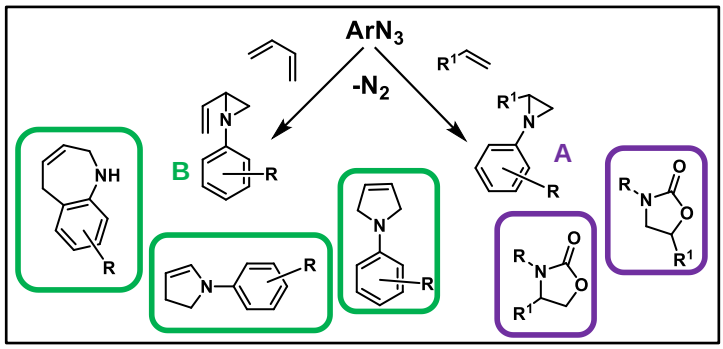
Sustainable synthesis of aziridines: versatile precursors of fine chemicals

Intrieri Daniela[a], *Carminati Daniela Maria*[a], *Gallo Emma*[a]

[a]*Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano (Italy); E-mail: daniela.intrieri@unimi.it*

The scientific community is greatly interested in the development of new methodologies to synthesise aziridines due to their pharmaceutical and biological properties (1). The use of atom efficient nitrene precursors, such as organic azides (RN_3), and efficient catalysts, such as metal porphyrins, could be an answer to society's demand for a more sustainable chemistry. For example, the activation of RN_3 by a metal catalyst forms the reactive fragment "RN" as well as N_2 as the only stoichiometric by-product (2).

In our group, porphyrin complexes have been extensively employed in batch conditions (3) to catalyse the synthesis of aziridines (**A**) and vinylaziridines (**B**), starting from alkenes and dienes, respectively. Considering that one of the main drawbacks of classic homogeneous catalysis is the catalyst recycling, we investigated the use of either catalytic membrane reactors (CMR) (4) or mesoreactors under continuous flow conditions (5) to increase the procedure sustainability.



When the aziridination was performed in CMR, aziridines were formed in very good yields and in several cases the membrane was reused with a low catalyst leaching and no decrease in reaction selectivities.

By using continuous flow conditions, yields and selectivities of ruthenium porphyrin-catalysed aziridinations were comparable to those achieved in batch conditions, while better performances and shorter reaction times were observed by using cobalt porphyrin catalysts. The flow system process was also successful in performing a two-step procedure in a single reactor where anilines were first transformed into aryl azides (Sandmeyer reaction) and then their reaction with styrenes yielded desired aziridines (5).

The study of the chemical reactivity of aziridines revealed that they are suitable starting materials for interesting fine chemicals such as benzoazepines (6) and oxazolidinones, which were obtained by aza-[3,3]-Claisen rearrangement of *N*-aryl-2-vinylaziridines and CO_2 cycloaddition reaction to aziridines, respectively.

References:

1. Yamaguchi J., Yamaguchi A.D. and Itami K.; *Angew. Chem. Int. Ed.*, **2012**, 8960-9009.
2. a) Fantauzzi S., Caselli A. and Gallo E.; *Dalton. Trans.*, **2009**, 5434-5443.; b) Intrieri D., Zardi P., Caselli A. and Gallo E.; *Chem. Commun.*, **2014**, 11440-11453.
3. Fantauzzi S., Gallo E., Caselli A., Piangiolino C., Ragaini F. and Cenini S.; *Eur. J. Org. Chem*., **2007**, 6053-6059.
4. Gallo E., Buonomenna M.G., Viganò L., Ragaini F., Alessandro Caselli A., Fantauzzi S., Cenini S. and Drioli E.; *J. Mol. Catal. A: Chem.*, **2008**, *282*, 85-91.
5. a) Rossi S., Puglisi A., Benaglia M., Carminati D. M., Intrieri D. and Gallo E.; *Cat. Sci. Tec.*, **2016**, 6, 4700-4704.; b) Rossi S., Puglisi A., Intrieri D. and Gallo E.; *J. Flow Chemistry*, **2016**, 243-239.; c) Intrieri D., S. Rossi S., Puglisi A. and Gallo E.; *J. Porphyrins and Phthalocyanines*, **2017**, in press.
6. Fantauzzi S., Gallo E., Caselli A., Piangiolino C., Ragaini F., Re N. and Cenini S.; *Chem. Eur. J.*, **2009**, *15*,1241-1251.

Aspects of the Functionalization of the Phosphorene Surface

Gabriele Manca[a], *Andrea Ienco*[a], *Maurizio Peruzzini*[a], *Carlo Mealli*[a]

[a]*Consiglio Nazionale delle Ricerche Istituto di Chimica dei Composti Organometallici*
Via Madonna del Piano 10, Sesto Fiorentino
gabriele.manca@iccom.cnr.it

Phosphorene, a 2D material derived from the exfoliation of layered black phosphorus, is appealing for potential applications and it is often compared to graphene in spite of quite different electronic properties.(1) Phosphorene is already a topic of great interest, although its functionalization is still scarcely proved experimentally, especially with transition metals.(2) The many P-lone pairs on the surface may imply high donor power toward unsaturated metals having mono- or poly-functional acceptor character. On the other hand, they are tilted by 30° out the perpendicular axis to the surface, requiring metal fragments having suitable empty σ hybrids. Nonetheless, mono-metallic species of formula L_nM (n = 1, 2 and 3 and M = d^{10}, d^8 and d^6, respectively) can be locally added to form an uncharged system with small L (*e.g.*, Cl^- or CO). The η^1, η^2 and η^3 coordination type were optimized at both molecular and periodic levels, as shown in Figure 1a-c, respectively. Remarkably, larger coligands determine hindrance problems for equivalent acceptor functionality of the metal. For instance, for L=PPh_3 the species with n= 2 or 3 cannot be formed because some bulky phenyl group are too close to the phosphorene's surface. Also, not all the metal fragments are equally suitable in spite of having equivalent acceptor capabilities. The systems have been analyzed also in terms of energy, including those of the interactions between two or more P_n layers to estimate the role of the dispersion forces in the assembly. Remarkably, the band gap increases on exfoliating the black phosphorus with some justification for its electronic underpinnings. Additionally, the behavior of DMSO as an exfoliating agent of black phosphorus has been explored with evidence of oxygen atom transfers to the surface. Analogously, other elements or groups (S or NR imido) similarly transfer from species such as Cl_3PS, S_8 or organic azides. Finally, also the behavior of I_2 has been monitored from the electronic and energy viewpoints in parallel with the different behavior of the diatomic toward the P_4 cage, which is fully demolished.

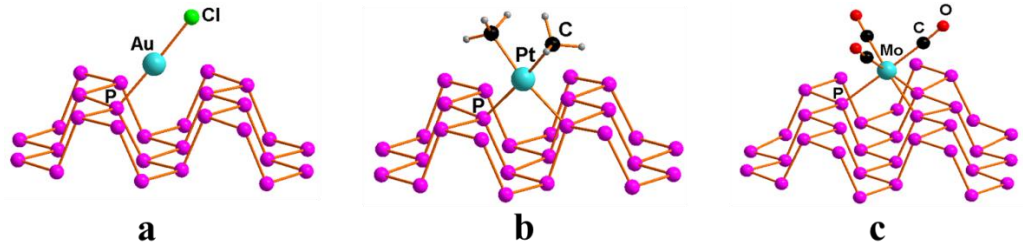


Figure 1. Functionalized phosphorene with metal fragments in: a) η^1, b) η^2 and c)η^3 coordination, respectively.

This work was supported by European Research Council through the ERC Advanced project PHOSFUN (Grant Agreement No. 670173).

References:1. Woomer, A. H.; Farnsworth, T. W.; Hu, J.; Wells, R. A.; Donley, C. L.; Warren, S. C. *ACSNano* **2015**, *9*, 8869-8884 and references within.2. Kulish, V. V.; Malyi, O.; Persson, C.; Wu, P. *Phys.Chem.Chem.Phys.* **2015**, *17*, 992-1000.

Polyesters from the Alternating Copolymerization of Epoxides and Cyclic Anhydrides

Mina Mazzeo,[a] *Florence Isnard,*[a] *Marina Lamberti*[a] *and Claudio Pellecchia*[a]

[a] *Department of Chemistry and Biology "A. Zambelli", University of Salerno, Via Giovanni Paolo II, 132*
84084 Fisciano (SA) Italy

Polyesters are amongst the most widely applied oxygenated polymers. They can be broadly divided into semiaromatic and aliphatic polyesters. Semiaromatic polyesters found application for the production of fibers, rigid plastics and engineering materials. Aliphatic polyesters, because of their biodegradability and biocompatibility, are the potentially sustainable alternatives to polymers derived from *fossil* sources and they find large application in biomedical field.

An efficient route for the syntheses of aliphatic polyesters is the ring-opening polymerization (ROP) of cyclic esters. (1) This method consents a punctual control of the microstructural parameters of the polymers allowing the synthesis of sophisticated macromolecular architectures (2, 3).

A more versatile way to produce polyesters, both aliphatic and semiaromatic, is the ring-opening copolymerization (ROCOP) of epoxides with cyclic anhydrides (4, 5). This method allows the access to a wide range of diverse polymer structures, thanks the availability to the two large distinct sets of monomers (3).

The most common catalysts described for this reaction generally feature a Lewis acid metal center penta-coordinated with salen or porphyrin ligands (4, 5). For all these catalysts, a complete selectivity of the procerss is reached only in the presence of a nucleophilic species that acts as co-catalyst.

Currently, the precise role of the co-catalyst remains rather obscure, but it is generally proposed that it coordinates to the metal center, promoting a dissociative mechanism resulting in the labilizing of the propagating polymer chain and accelerating polymerization.

We speculated that reactive aluminum centers with lower coordination, permitting the simultaneous coordination of the nucleophilic cocatalyst and the incoming monomer, could promote more the reaction rate (6 and 7). Thus, we decided to investigate the catalytic behavior in the copolymerization of epoxides with cyclic anhydrides of different tetra-coordinated aluminum complexes supported by phenoxy-imine and phenoxy-amine ligands

For all complexes, we observed catalytic activities much higher than those reported for the related penta-coordinated aluminum complexes. The structure-activity relationship of diverse monometallic hemi-salen complexes was also rationalized.

Subsequently, the structure of the ancillary phenoxy-imine ligand was modify by introducing an additional pendant donor able to simulate the function of the co-catalyst. This complex was able to promote perfectly selective polymerization without the addition of a hexogen co-catalyst. This complex represents the first example of bifunctional aluminum catalyst for the selective copolymerization of epoxides and anhydrides.

References:

1.Dubois, P; Coulembier, O.; Raquez, J. M. Handbook of ring-opening polymerization. John Wiley & Sons, 2009. 2.P. J. Dijkstra, Hongzhi Du and Jan Feijen Polym. Chem, 2011, 2, 520–527. 3.Pilone,A.; Press, K.; Goldberg, I.; Kol, M.; Mazzeo, M.; Lamberti, M.; J. Am. Chem. Soc., 2014, 136, 2940–2943. 4. Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. *Chem. Commun.*, 2015, 51, 6459-6479. 5.Longo, J. M.; Sanford, M. J.; Coates, G. W.; *Chem. Rev.* 2016, 116, 15167–15197. 6.Isnard, F.; Lamberti, M.; Lettieri, L.; D'auria, I.; Press, K.; Troiano, R.; Mazzeo, M. *Dalton Trans.*2016, 45, 16001-16010.7.Isnard, F., Lamberti, M., Pellecchia C. & Mazzeo, M. (2017), *ChemCatChem.* DOI 10.1002/cctc.201700234R1.

Water Oxidation catalyzed by Ir(III) and Ru(III)-doped hydrotalcite-like compounds

Lucia Fagiolari [a], *Greta Patzke* [b], *Alceo Macchioni* [a]

[a] *University of Perugia (Italy). Department of Chemistry, Biology and Biotechnology. Via Elce di Sotto 8, 06123 Perugia (Italy);* [b] *University of Zurich. Department of Chemistry. Winterthurerstrasse 190, 8057 Zurich (Switzerland); lucia.fagiolari@studenti.unipg.it*

Water oxidation (WO) is considered the bottleneck for the development of an artificial photosynthetic apparatus aimed at the green production of renewable fuels(1). Over the last few years, many molecular(2), heterogeneous(3) and heterogenized(4) catalysts have been reported. Furthermore, we demonstrated that a ternary system constituted by an Ir(III)-doped ZnAl hydrotalcite-like compound (HTlc) is an efficient and recyclable heterogeneous WO catalyst(5). Particularly, we showed that $[Zn_{0.667}Al_{0.306}Ir_{0.027}(OH)_2]Cl_{0.333}\bullet 0.4H_2O$ is capable of catalyzing WO with top performance both in terms of TOF (up to 113 min^{-1}) and TON (> 11900), in the presence of $NaIO_4$ as the sacrificial oxidant(5). Herein, we show that both Ir(III) and Ru(III)-doped HTlcs are efficient and robust heterogeneous catalysts for water oxidation also in electrocatalytic experiments. The HTlc presented here have zinc or magnesium as the bivalent cation and aluminum as the trivalent one. Two of them were doped with Ir(III) and one with Ru(III) ions, via an isomorphic replacement of Al(III) ions. Their chemical formulas, determined by ICP-OES analysis, are: $[Zn_{0.647}Al_{0.349}Ir_{0.004}(OH)_2](Cl)_{0.353}\bullet xH_2O$ (**1**), $[Mg_{0.647}Al_{0.349}Ir_{0.004}(OH)_2](CO_3)_{0.177}\bullet xH_2O$ (**2**) $[Zn_{0.650}Al_{0.330}Ru_{0.020}(OH)_2](Cl)_{0.350}\bullet xH_2O$ (**3**). The brucitic structure is retained after the incorporation of the noble metal that was found to be homogeneously distributed throughout the sample, as confirmed by X-ray diffranction patterns and SEM-EDX images. The performances of the HTlcs toward water oxidation have been evaluated in a standard three electrode-apparatus (KOH 1M), immobilizing the catalysts in carbon paste electrodes. Interstingly, **1** and **3** show a lower overpotential (352mV *vs* 388mV at 10mA/cm^2) and twice as high current density with respect to IrO_2 (2.1 *vs* 1.2 mA/cm^2 at 280mV), used as benchmark (Fig.1). Instead, **2** shows a current density comparable to that of IrO_2. In addition, long-term stability tests, such as chronoamperometry and chronopotentiometry, show that these catalysts are not only stable under the catalytic conditions used, but also their performances increase over time.

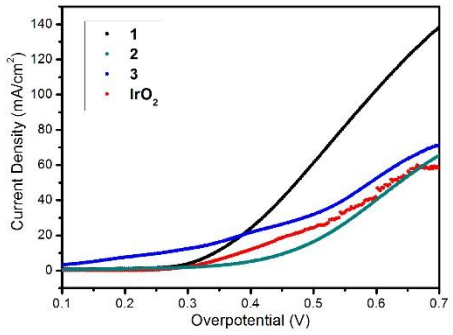


Fig. 1 Linear Sweep Voltammetry curves of **1**, **2**, **3** and IrO_2 collected at a scan rate of 1mV/s, in KOH 1M

References: 1. Balzani, V.; Credi, A.; Venturi, M.; *ChemSusChem*, **2008**, 1, 26-58. 2. Kärkäs, M.D.; Verho, O.; Johnston, E.V.; Åkermark, B.; *Chem. Rev.* **2014**, 114, 11863-12001. 3. Osterloh, F.E.; *Chem. Mater*. **2008**, 20, 35-54. 4. Savini, A.; Bucci, A.; Nocchetti, M.; Vivani, R.; Idriss, H.; Macchioni, A.; *ACS Catal*. **2015**, 5, 264-271. 5. Fagiolari, L.; Scafuri, A.; Costantino, F.; Vivani, R.; Nocchetti, M.; Macchioni, A.; *ChemPlusChem* **2016**, 81, 1060-1063.

New Self-Assembling Luminescent Materials from Pyridyl Oxadiazole Zn(II) Complexes

Diana Rosita [a], Borbone Fabio [a], Caruso Ugo [a], Concilio Simona [b], Piotto Stefano [b], Panunzi Barbara [c]

[a]Department of Chemical Science, University of Napoli "Federico II", Cupa Nuova Cintia, 21 - 80126 – Napoli, Italy;

[b]Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy;

[c]Department of Pharmacy, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy

[d]Department of Agriculture, University of Napoli Federico II, via Università 100, 80055 Portici, NA, Italy

E-mail: rosita.diana@libero.it

In the last years, a large number of papers have been published from our laboratories on zinc complexes from polydentate ligands, their interest due both to their fascinating structural topologies and the potential applications in sensing, photoluminescence and optoelectronic (1,2). In some cases, the assembling of suitable ligands and/or preformed polymeric chains with Zn(II) proved to be an efficient route for the formation of metallated polymeric materials whose photoluminescence properties were examined in correlation with structural data (3,4). In particular, self-assembling of small building blocks by coordination to the metal centers can generate polymers or networks. Recently, interest has increased on self-assembling metal containing structures where weak metal-ligand interactions easily allow to obtain materials with specific desirable properties, offering a convenient alternative to the conventional preparation of macromolecules by covalent bond formation (5,6).

We now report the synthesis of zinc-mediated self-assembling luminescent materials from pyridyl oxadiazol 2-phenol ligands (Figure 1).

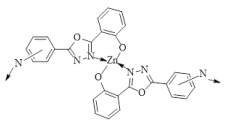


Figure 1

As expected, ligands act as mononegative chelates in mononuclear Zn(II) tetracoordinated complexes. The presence of the pyridyl moiety produces an additional potential coordination site whose role can be tuned by changing position of the nitrogen in the ring.

In all cases, by spectroscopic studies, no interactions were detected in solution, making the system soluble and processable. On the other hand, in the solid state N-Zn weak interactions cause the assembling of the isolated complexes in a non-structured network. Strong and stable glasses were obtained by spin-coating or casting of complex solutions, giving in some cases highly luminescent films. PLQY values measurements and theoretical analysis complete the study of this systems.

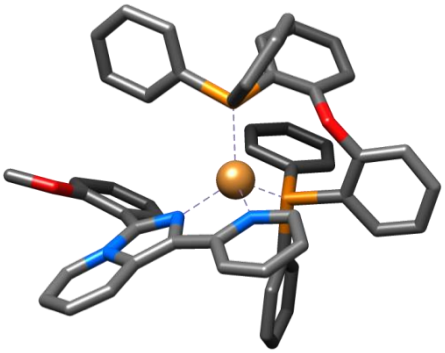
1. European Journal of Inorganic Chemistry 2014 (34), 5916-5924; Argeri, Mario; Borbone, Fabio; Caruso, Ugo; Causà, Mauro; Fusco, Sandra; Panunzi, Barbara; Roviello, Antonio; Shikler, Rafi; Tuzi, Angela. 2. European Journal of Inorganic Chemistry 2014 (16), 2695; Borbone, Fabio; Caruso, Ugo; Causa, Mauro; Fusco, Sandra; Panunzi, Barbara; Roviello, Antonio; Shikler, Rafi; Tuzi, Angela. 3. European Journal of Inorganic Chemistry 2016 (6), 818-825; Borbone, Fabio; Caruso, Ugo; Concilio, Simona; Nabha, Shiran; Panunzi, Barbara; Piotto, Stefano; Shikler, Rafi; Tuzi, Angela.4. Inorganic Chemistry Communications 2013 (38), 135-138; Borbone, Fabio; Carella, Antonio; Roviello, Giuseppina; Ricciotti, Laura; Panunzi, Barbara; Catauro, Michelina; Roviello, Antonio.5. Journal of Materials Chemistry. 2012 (22), 6218-6231; Lim, Zheng Bang; Li, Hairong; Sun, Shuangyong; Lek, Jun Yan; Trewin, Abbie; Lama, Yeng Ming; Grimsdale, Andrew C. 6. Inorganic Chemistry Communication 2010 (13), 809-813; Song, Zhi-Gang; Geng, Cui-Hong; Ma, Jian-Ping; Dong, Yu-Bin.

Luminescent complexes and their bright ligands

Claudio Garino[a], Giorgio Volpi[a], Claudia Barolo[a], Roberto Gobetto[a], Carlo Nervi[a], Michael D. Weber[b], Rubén D. Costa[b]

[a] Department of Chemistry, University of Turin, Via Giuria 7, I-10125 Torino, Italy; [b] Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg (FAU) Egerlandstr 3, D-91058 Erlangen, Germany

Luminescent transition metal complexes are of great interest for the development of probes, sensors, electroluminescent materials, light-harvesting materials, photocatalysts, and so on.
Their electronic absorption and luminescence properties can, in principle, be fine-tuned by an appropriate choice of the central metal and of the coordinated ligands, however rationalizing the structure-property relationships is not straightforward.
This contribution provides a brief overview on the photophysical features of a series of transition metal complexes containing as ligands organic molecules that are themselves luminescent. In particular, the attention is focused on the use of pyridinylimidazo[1,5-a]pyridine derivatives, a class of aromatic heterocyclic compounds widely reported in literature for its optical properties (1,2).



Adopted with the aim of obtaining highly emitting complexes, the coupling of pyridinylimidazo[1,5-a]pyridines and transition metals such as Cu, Re Ir resulted in complexes displaying unconventional and counterintuitive emission properties (3,4,5,6) that can be somewhat rationalized recalling the intersystem crossing between low-lying singlet and triplet excited states localized at the bidentate ligand bound directly to a heavy metal atom (7).

References: 1. Weber M.D., Garino C., Volpi G., Casamassa E., Milanesio M., Barolo C., Costa R.D., *Dalton Trans.*, 2016, 45, 8984. 1. Volpi G., Garino C., Conterosito E., Barolo C., Gobetto R., Viscardi G., *Dyes Pigments* 2016, *128*, 96. 2. Volpi G., Garino C., Priola E., Diana E., Gobetto R., Buscaino R., Viscardi G., Barolo C., *Dyes Pigments* 2017, *143*, 284. 3. Garino C., Ruiu, T., Salassa L., Albertino A., Volpi G., Nervi C., Gobetto R., Hardcastle K.I., *Eur. J. Inorg. Chem.* 2008, *23*, 3587. 4. Salassa L., Garino C., Albertino A., Volpi G., Nervi C., Gobetto R., Hardcastle K.I., *Organometallics* 2008, *27*, 1427. 5. Volpi G., Garino C., Salassa L., Fiedler J., Hardcastle K.I., Gobetto R., Nervi C., *Chem.- Eur. J.* 2009, *15*, 6415. 6. Weber M.D., Garino C., Volpi G., Casamassa E., Milanesio M., Barolo C., Costa R.D., *Dalton Trans.* 2016, *45*, 8984. 7. Blanco-Rodríguez A.M., Kvapilova H., Sykora J., Towrie M., Nervi C., Volpi G., Zalis S., Vlcek A., *J. Am. Chem. Soc.* 2014, *136*, 5963.

Layer by layer order of molecular thin films detected by Torque Magnetometry

Mauro Perfetti[a*], *Michele Serri*[a], *Lorenzo Poggini*[a], *Matteo Mannini*[a], *Donella Rovai*[a], *Philippe Sainctavit*[b], *Sandrine Heutz*[c] *and Roberta Sessoli*[a]

[a] *Department of Chemistry "U. Schiff" Università di Firenze and INSTM RU Firenze, Via della lastruccia 3-13, 50019 Sesto Fiorentino (IT);* [b] *Synchrotron SOLEIL L'Orme des Merisiers Saint Aubin, 91192 Gif-sur-Yvette, (FR);* [c] *Department of Materials and London Centre of Nanotechnology, Imperial College London, SW7 2AZ London (UK); *present address: Department of Chemistry, University of Copenhagen, Universitetparken 5, 2100 Copenhagen (DK). E-mail: mauro.perfetti@chem.ku.dk*

Thin layers composed by magnetic molecules, have attracted considerable interest in the scientific community for application in the fields of quantum computation (1), information storage (2) and spintronics (3). However, before proceeding with any kind of application, a detailed knowledge of the molecular order is mandatory. The technique that are commonly used to obtain this information are however often limited by the penetration length of the radiation used as a probe (usually few nm), or are only able to deliver an average orientation of the film.

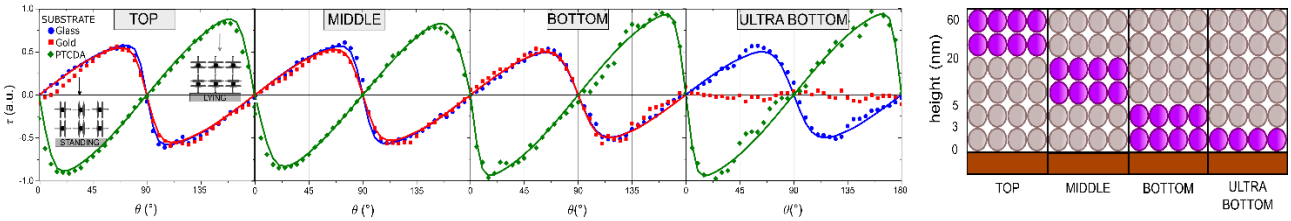


Figure 1. Left: CTM curves of samples composed by $TbPc_2$ and YPc_2 layers at different height (see figure on the right: violet spheres represent $TbPc_2$ and grey spheres represent YPc_2).

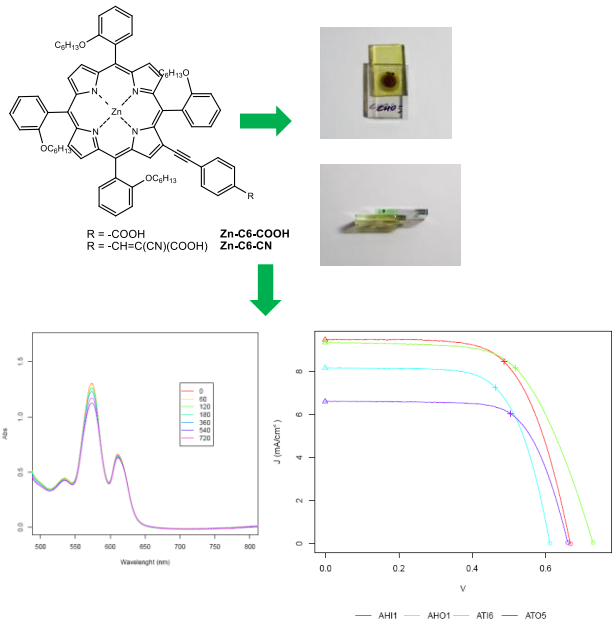
To overcome this limitation, we exploited the peculiar sensitivity of Cantilever Torque Magnetometry to magnetic anisotropy (4). Indeed, we measured several samples composed by $LnPc_2$ (Bis-phthalocyaninato neutral complex, where Ln=Tb or Y) molecules evaporated on three different substrates (glass, gold and perylene-3,4,9,10-tetracarboxylic dihanidride, PTCDA). Since YPc_2 is diamagnetic and isotropic, CTM is able to selectively detect the order of the $TbPc_2$ molecules that were evaporated at different distance from the substrate. Collecting information of four different samples, we were able to precisely reconstruct the packing of molecules from the first layers up to hundreds of nanometers. To reproduce the experimental points, we developed a code that is able to include a Gaussian molecular distribution centred on the most probable orientation. On glass, the molecules assumed a standing configuration (Pc rings perpendicular to the surface) while on PTCDA a lying configuration (Pc rings parallel to the surface) was imposed by the strong interaction between the highly-conjugated substrate and the Pc rings. The case of the gold substrate was more complex: the first layer assumed a lying configuration that rapidly turned into a standing configuration due to the competing effect between favorable interaction with the substrate and π–π interactions. This study opens the possibility to use anisotropic molecules as local probes to detect order in surface or buried layers of molecular thin films (5).

References: 1. Ladd T.L. *et al.*, Nature, **2010**, *464*, 7285 2. Mannini M. *et al.*, Nature Materials, **2009**, *8*, 194 3. Bogani L. *et al.*, Nature Materials, **2008**, *7*, 179 4. Perfetti M. *et al.*, Chem. Eur. J. **2014**, *20*, 14051. 5. Perfetti M. *et al.*, Adv. Mater. **2016**, *28*, 6946.

Porphyrin-Sensitized Solar Cells: the challenge of photostability

Francesca Tessore[a], *Gabriele Di Carlo*[a], *Alessio Orbelli Biroli*[b], *Maddalena Pizzotti*[a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Unità di Ricerca dell'INSTM, via C. Golgi 19-20133 Milano (Italy);* [b] *Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), SmartMatLab Centre, via C. Golgi 19-20133 Milano (Italy); francesca.tessore@unimi.it*



Dye-sensitized solar cells (DSSC) are a highly promising alternative to conventional photovoltaic silicon-based devices (1). A key-role is played by the dye and porphyrin sensitizers have drawn great interest because of their excellent light-harvesting properties mimicking photosynthesis (2, 3). In 2014 a device based on a D-π-A Zn^{II} porphyrin with a $[Co(bpy)_3]^{2+/3+}$ redox couple attained an unprecedented photon-to-current conversion efficiency (PCE) of 13.0% (4), higher than that reported for the best Ru(II)-based dyes traditionally employed in DSSC. However, a still quite unexplored topic is the stability towards photodegradation of Porphyrin Sensitized Solar Cells (2), an issue of outstanding importance for their potential application in Building Integrated Photovoltaics (BIPV), for which the greenish color displayed by porphyrin complexes could be very appealing (5).

Therefore two β-substituted Zn^{II}-tetraarylporphyrins, bearing hexyloxy chains ($–OC_6H_{13}$) in the *ortho*-position of each aryl ring (so to prevent detrimental π-π aggregation) and a carboxylic or a cyanoacetic acceptor group (to be anchored to TiO_2 surface) have been synthesized. Thanks to the facilities of the SmartMatLab Centre hosted by the Department of Chemistry of the Università degli Studi di Milano (6), prototype solar cells of both dyes have been assembled on FTO glasses (1.25x2.0 cm, with an active area of 0.196 cm^2) coated with a 6 μm thick transparent TiO_2 layer (20 nm nanoparticles), in air or under nitrogen atmosphere, uptaking the dye by two different solvent mixtures (EtOH:THF = 9:1 or EtOH:toluene=1:1), and using a I^-/I_3^- redox couple. Some cells have been coated also with a UV filter adhesive film purchased by Solaronix. The photostability of the devices has been evaluated through UV-Vis spectroscopy after radiation of the solar cells with a Solar Simulator (under 1 sun illumination through an AM 1.5G filter), monitoring the changes in absorption maximum and intensity of the Q bands of the dye after regular time intervals (0', 90',180', 240', 300', 360', 540', 720', 900', 1080', 1260', 1440', 1620' and 1800'). Moreover, the starting PCE of the cells have been compared to that after 1800' irradiation.

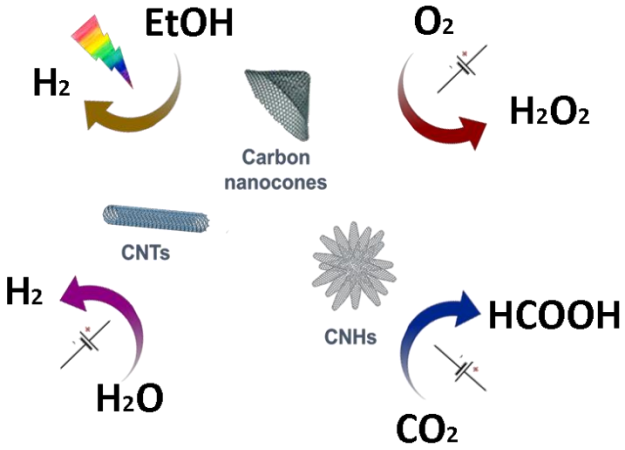
References: 1. O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. 2. Diau, E. G. –W.; Li, L. –L. *Chem. Soc. Rev.* **2013**, *42*, 291. 3. Urbani, M.; Grätzel, M.; Nazeeruddin, M. K.; Torres, T. *Chem. Rev.* **2014**, *114*, 12330. 4. Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. *Nat. Chem.* **2014**, *6*, 242. 4. 5. Yoon, S.; Tak, S.; Kim, J.; Jun, Y.; Kang, J. *Build. Environ*. **2011**, *46*, 1899. 6. http://users2.unimi.it/smartmatlab/wordpress/

Hierarchical materials based on carbon nanostructures as advanced catalysts in energy applications

Michele Melchionna[a], *Francesco Paolucci*,[b] *Marcella Bonchio*,[c] *Francesco Vizza*,[d] *Paolo Fornasiero*,[a] *Maurizio Prato*,[a]

[a] *Department of Chemical and Pharmaceutical Sciences and INSTM, via L. Giorgieri 1, 34127 Trieste (Italy);* [b] *Department of Chemistry 'Giacomo Ciamician', University of Bologna and INSTM, via Selmi 2, Bologna 40126;* [c] *ITM-CNR and Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, 35131 Padova, Italy;* [d] *ICCOM-CNR, via Madonna del Piano 10, 50019, Sesto Fiorentino (FI) (Italy).*
melchionnam@units.it

Carbon nanostructures (CNSs) have emerged as unique building blocks in the assembly of complex functional materials. Heterogeneous catalysis is one particular field where the intriguing properties of CNSs can be fruitfully exploited (1). This contribution provides a glimpse of the results of the last 3 years within our group on the synthesis of new hierarchical materials based on CNSs and their application in modern key energy processes. In particular, two types of nanomaterials are discussed, one featuring a hierarchical ternary nanohybrid integrating CNSs (carbon nanotubes, nanohorns and nanocones), Pd nanoparticles and TiO_2, and the other consisting of a metal free hierarchical carbon material appropriately doped with N atoms. The fully characterized materials have shown excellent performance in photocatalytic H_2 production (2,3), as well as in the electrocatalytic hydrogen evolution reaction (4), CO_2 reduction (5) and selective oxygen reduction to hydrogen peroxide (6).



References:
1. M. Melchionna, M. Bonchio, F. Paolucci, M. Prato and P. FornasieroTopics Curr. Chem. 2014, 348, 139-180
2. A. Beltram, M. Melchionna, T. Montini, L. Nasi, M. Prato, and P. Fornasiero. Green Chem. 2016, DOI: 10.1039/C6GC01979J1. 3. M. Melchionna, A. Beltram, T. Montini, M. Monai, L. Nasi, P. Fornasiero, M. Prato. Chem. Commun. 2016, 52, 764-767.4. G. Valenti, A. Boni, M. Melchionna, M. Cargnello, L. Nasi, G. Bertoni, R. J. Gorte, M. Marcaccio, S. Rapino, M. Bonchio, P.Fornasiero, M. Prato and F. Paolucci Nat. Commun. 2016, 7, article number: 13549.5. M. Melchionna, M. V. Bracamonte, A. Giuliani, L. Nasi, T. Montini, C. Tavagnacco, M. Bonchio, P. Fornasiero, M. Prato (paper submitted)6. D. Iglesias, A. Giuliani, M. Melchionna1, S. Marchesan, A. Criado, L. Nasi, M. Bevilacqua, C. Tavagnacco, F. Vizza, P. Fornasiero, M. Prato (paper submitted)

Pyran based dyes as photosensitizers for p-type dye-sensitized solar cells

Antonio Carella [a], *Roberto Centore*[a], *Matteo Bonomo*[b], *Danilo Dini*[b], *Aldo Di Carlo*[c].

[a] *Dept. of Chemical Sciences, University of Naples Federico II, Complesso Universitario Monte Sant'Angelo, via Cintia, 80126 Naples (Italy);* [b] *Dept. of Chemistry, University of Rome "La Sapienza", p.le Aldo Moro 5, 00185 Rome (Italy) ;* [c] *Centre for Hybrid and Organic Solar Energy (CHOSE), Dept. of Electronic Engineering, University of Rome "Tor Vergata", via del Politecnico 1, 00133 Rome (Italy); antonio.carella@unina.it*

The heart of a dyes-sensitized DSSC device is a wide bandgap semiconductor oxide, sensitized with a photoactive dye able to inject, upon photoexcitation, electrons (*n*-type) or holes (*p*-type) in the semiconductor substrate (1). While *n*-type DSSC have been thoroughly investigated and a power conversion efficiency (PCE, η) exceeding 14 % have been reached (2), the number of studies regarding *p*-type DSSCs is significantly lower; it is anyway increasing in the last years because these kinds of devices open the way to the realization of tandem DSSC device based on the connection of a *p*-type photoelectrode with a *n*-type photoelectrode, each contributing to the total photovoltage generated by the cell (3). So far, the performances of *p*-DSSCs remain a way lower (4) than the *n*-type counterparts and a great work of optimization of different is still required. For what concerns the sensitizers different requirements as absorption in a broad range of the solar spectrum along with high molar extinction coefficients are needed. Moreover, it is essential that, upon photoexcitation, electron density moves away from the anchoring points on semiconductor oxide surface so that charge recombination occurs at lower rate. In this context, we investigated the properties of pyran based dyes, featuring, as shown in Figure 1, a similar molecular structure: the dyes are based on a pyran core functionalized with electron acceptor groups of different strengths and symmetrically coupled to carbazole or phenothiazine donor branches. Donor branches are functionalized with carboxylic group to allow a firm adhesion on the semiconductor oxide surface in the device assembling. Optical properties of the dyes are deeply influenced by the nature of the electron-acceptor group, so that the overall absorption of the reported dyes covers most of the visible spectrum. The properties of devices based on the NiO electrodes sensitized with the investigated dyes were evaluated under simulated solar radiation: the larger short circuit current density exceeded 1 mA/cm^2 and power conversion efficiency as high as 0.07 % could be recorded.

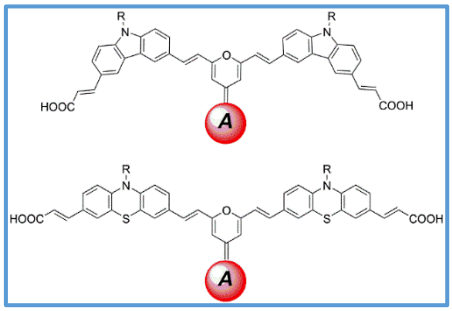


Figure 1. *Molecular structure scheme of the reported dyes*

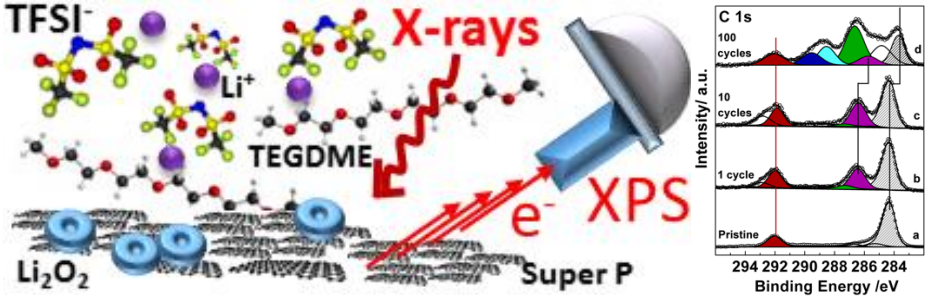
References: 1. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110 (2010) 6595. 2. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i- Fujisawa, M. Hanaya, Chem. Commun., 51 (2015) 15869. 3. C.J. Wood, G.H. Summers, E.A. Gibson, Chem. Commun. 51 (2015) 3915. 4. F. Odobel, Y. Pellegrin, J. Phys. Chem. Lett. 4 (2013) 2551

Unravelling the surface degradation mechanisms in ether electrolyte based Li-O_2 cells

Andrea G. Marrani[a], *Daniela Giacco*[a], *Robertino Zanoni*[a], *Sergio Brutti*[b]

[a] *Dip. Chimica, "Sapienza" Università di Roma, p.le Aldo Moro 5, Rome, Italy ;* [b] *Dip. Scienze, Università della Basilicata, V.le Ateneo Lucano 10, Potenza, Italy*

Li-air cells are at the cutting edge among the devices for energy storage (1-3). The electrode reactions, called Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER), occur on discharge and charge at the triple interface O_2/cathode/electrolyte. The use of a stable lithium salt (e.g. lithium bis(trifluoromethane sulfonyl) imide, LiTFSI) dissolved in an ethereal solvent (e.g. tetraethylene glycol dimethyl ether, TEGDME) as aprotic electrolyte leads to the reversible formation of lithium peroxide (Li_2O_2) as main discharge product (1-3). A carbon paper has usually been used as cathode material for Li-air cells due to its favorable matching with various desired characteristics (high porosity and surface area, high anodic stability, lightness, availability, low cost etc.). However, carbon has shown low inertness to chemical oxidative attacks from reduced forms of oxygen (O_2^-, O_2^{2-}, LiO_2, Li_2O_2). We have recently reported about the long-term fading of performance of Li-air cells assembled with a carbon cathode and an ether-based electrolyte due to the carbon paper and/or the TEGDME chemical instability (4,5). Carbon paper cathodes were discharged/cycled vs. lithium by potential and/or capacity limited galvanostatic cycling using the couple LiTFSI/TEGDME as electrolyte. After the electrochemical measurements, the cathodes were analyzed by means of XPS, FTIR, SEM/TEM. This multi-technique characterization approach allowed us to explore the complex surface composition of the samples with particular emphasis on degradation issues.



In the search for a stable cathode material for Li-air cells, our experimental activity is now focused on carbon-free electrodes. Within this family, $NiCo_2O_4$ is well known for its bifunctional electrocatalytic activity towards the ORR and the OER (6,7). A set of novel M^{n+}-doped $NiCo_2O_4$@Ni (M^{n+} = Cr^{3+}, Cu^+, Zn^{2+} etc.) foam cathode materials for Li-air cells is presented here. These materials were synthesized by means of hydrothermal method. Our aim is to clarify the dopants influence on the electrochemical performance and to assess the enhancement of cell stability when TEGDME is in contact with these novel cathode materials.

References: 1. N. Feng, P. He and H. Zhou, Adv. Energy Mater., 2016, 6, 1–24. 2. N. Imanishi, A. C. Luntz and P. Bruce, The Lithium Air Battery: Fundamentals, Springer, New York, 2014. 3. J. Lu, L. Li, J. Park, Y. Sun, F. Wu and K. Amine, Chem. Rev., 2014, 7, A-AD. 4. M. Carboni, S. Brutti and A. G. Marrani, ACS Appl. Mater. Interfaces, 2015, 7, 21751-21762. 5. D. Giacco, M. Carboni, S. Brutti, A. G. Marrani, submitted. 6. D.U. Lee, B. J. Kim and Z. Chen, J. Mater. Chem. A, 2013, 1, 4754-4762. 7. X. Lin, J. Su, L. Li and A. Yu, Electrochimica Acta, 2015, 168, 292-299.

Networks based on functionalized noble metal nanoparticles: advanced materials for optical and electronic applications

Ilaria Fratoddi[a], *Iole Venditti*[a], *Laura Fontana*[a], *Concita Sibilia*[b], *Grigore Leahu*[b], *Alessandro Belardini*[b], *Roberto Li Voti*[b], *Chiara Battocchio*[c], *Roberto Matassa*[d]; *Giuseppe Familiari*,[d]

[a] *Department of Chemistry, University of Rome La Sapienza ;* [b] *Department of S.B.A.I. University of Rome La Sapienza ;* [c] *Department of Science, Roma Tre, University of Rome;* [d] *Department of Anatomical, Histological, Forensic and Orthopaedic Sciences, Section of Human Anatomy. University of Rome Sapienza, Rome Italy; ilaria.fratoddi@uniroma1.it*

A wide range of advanced applications are based on noble metal nanoparticles (MNPs), because of their unique chemical and physical properties and versatile synthesis, that allows to functionalized metal surface with optically active organic or organometallic molecules.(1,2) In particular, the research in biomedicine, catalysis, energy conversion and sensors are strongly influenced by these materials (3,4). The colloidal MNPs can be manipulated to induce self-assembly into complex structures, 2D or 3D networks that show collective properties (5). In this work platinum, palladium, gold and silver nanoparticles (PtNPs, PdNPs, AuNPs, AgNPs) have been synthesized in the presence of different bifunctional thiols; the prepared MNPs have been characterized with spectroscopic and morphological techniques and by means optical and electrical conductivity measurements. In particular, the obtained AuNPs have shown a diameter of about 5-10 nm and a spherical shape (see Fig.1), showing the typical Surface Plasmon Resonance (SPR) of the system that was found at 520 nm. For AgNPs dimension are around 3-5 nm, with SPR at 430 nm. The MNPs showed interesting results regarding the electrical conductivity measurements, carried out at room temperature, in dark conditions and under visible light: the AuNPs showed a nonohmic behavior whereas the AgNPs an ohmic one.

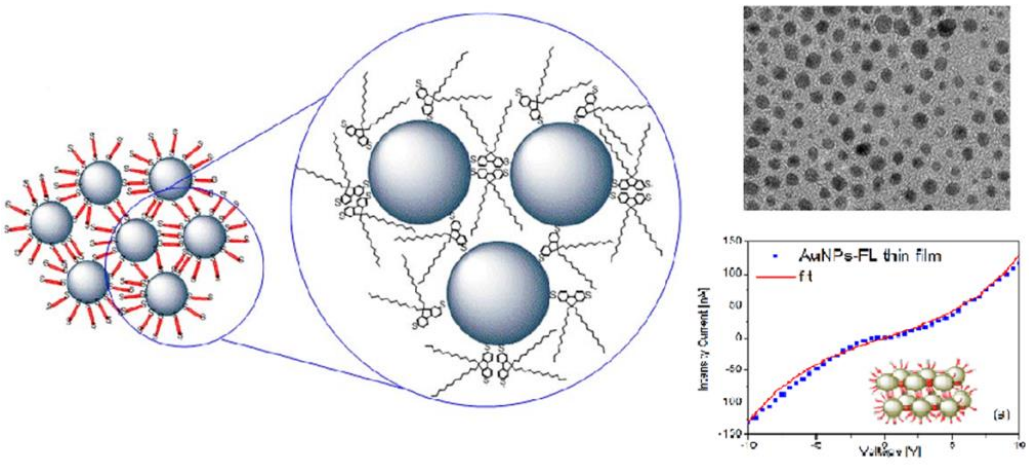


Fig.1. MNPs based network; TEM image and electrical characterization.

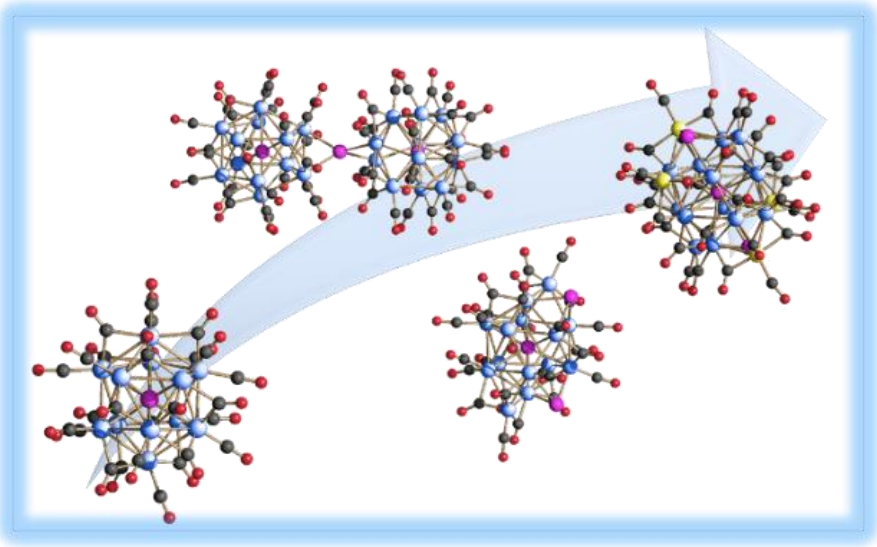
References: 1. Zhang, Y., Manjavacas, A., Hogan, N. J., Zhou, L., Ayala-Orozco, C., Dong, L., Halas, N. J. Nano letters, 2016, 16, 3373-3378. 2. Quintiliani, M., Bassetti, M., Pasquini, C., Battocchio, C., Rossi, M., Mura, F., Matassa, R., Fontana, L., Russo, MV, Fratoddi, I. Journal of Materials Chemistry C, 2014, 2, 2517-2527. 3. Fratoddi, I., Venditti, I., Cametti, C., Russo, M.V. Nano Research 2015, 8, 1771-1799. 4. Fratoddi, I., Macagnano, A., Battocchio, C., Zampetti, E., Venditti, I., Russo, M. V., Bearzotti, A Nanoscale, 2014, 6(15), 9177-9184. 4. 5. Ghosh, S.K., Pal, T. Chem. Rev. 2007, 107, 4797-4862.

New examples of interstitial Bismuth atoms in icosahedral rhodium cages

Cristina Femoni[a], *Guido Bussoli*[a], *Iacopo Ciabatti*[a], *Marco Ermini*[a], *Mohammad Hayatifar*[b], *Maria C. Iapalucci*[a], *Silvia Ruggieri*[a], *Stefano Zacchini*[a].

[a] *Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento, 4 – Bologna.;* [b] *Italiëlei 235, 2000 Antwerpen – Belgium*

The chemistry of homo-metallic carbonyl clusters of rhodium has been widely investigated over the last four decades. (1, 2) The capability of rhodium compounds to interstitially host light *p* elements, such as C and N, gave rise to the fruitful chemistry of carbide and nitride Rh clusters. (3) However, less has been achieved when moving to heavier post-transition elements, and only a few examples are known so far, among which $[Sb@Rh_{12}(CO)_{27}]^{3-}$ (4, 5) and $[Sn@Rh_{12}(CO)_{27}]^{4-}$. (6) In order to widen the chemistry of rhodium compounds containing post-transition elements, we investigated the chemistry of hetero-metallic Rh-Bi carbonyl clusters. The reaction of $[Rh_7(CO)_{16}]^{3-}$ with $BiCl_3$ under N_2 and at room temperature results in the formation of the new hetero-metallic $[Bi@Rh_{12}(CO)_{27}]^{3-}$ cluster in high yields. Further controlled addition of $BiCl_3$ leads firstly to the formation of the dimeric $[(Bi@Rh_{12}(CO)_{26})_2Bi]^{5-}$ and the *closo*-$[Bi@Rh_{14}(CO)_{27}Bi_2]^{3-}$ species in low yields, and finally, to the $[Bi@Rh_{17}(CO)_{33}Bi_2]^{4-}$ cluster. All clusters have been spectroscopically characterized by IR and ESI-MS spectrometry, and their molecular structures fully determined by X-ray diffraction studies. Notably, they represent the first examples of Bi atoms interstitially lodged in metallic cages that, in this specific case, are all based on an icosahedral geometry. Moreover, $[Bi@Rh_{14}(CO)_{27}Bi_2]^{3-}$ forms an exceptional network of infinite zig-zag chains in the solid state, thanks to intermolecular Bi-Bi distances.



1. Dolzhnikov, D. S.; Iapalucci, M. C.; Longoni, G.; Tiozzo, C.; Zacchini, S; Femoni, C. *Inorg. Chem*. **2012**, *51*, 11214-11216.
2. Martinengo, S.; Ciani, G.; Sironi, A. *J. Am. Chem. Soc*. **1980**, *102*, 7564-7565.
3. Hughes, A. K.; Wade, K. *Coord. Chem. Rev*. **2000**, *197*, 191–229.
4. Vidal, J. L.; Troup, J. M. *J. Organomet. Chem*. **1981**, *213*, 351-363.
5. Femoni, C.; Ciabatti, I.; Iapalucci, M. C.; Ruggieri, S.; Zacchini S. *Progr. Nat. Sci.: Mat. Int.* **2016**, *26*, 461-466.6. Femoni, C.; Iapalucci, M. C.; Longoni, G.; Tiozzo, C.; Zacchini, S.; Heaton, B. T.; Iggo J. A. *Dalton Trans*. **2007**, *35*, 3914-3923.

Synthetic Strategies Towards Quantum Coherence Time Enhancement in Potential Molecular Spin Qubits

M. Atzori[a], *L. Tesi*[a], *E. Morra*,[b] *M. Chiesa*,[b] *L. Sorace*,[a] *R. Sessoli*[a]

[a] *LAboratory of Molecular Magnetism, Dipartimento di Chimica "Ugo Schiff" & INSTM RU, Università degli Studi di Firenze, Sesto Fiorentino (FI) - Italy;* [b] *Dipartimento di Chimica & NIS Centre, Università di Torino, Torino - Italy; matteo.atzori@unifi.it*

The preparation and characterization of magnetic molecules that behave as potential molecular spin qubits represent a fundamental step to evaluate the viability of such systems in the field of quantum information processing (1,2). In this regard, mononuclear vanadium(IV) complexes have been identified among the best performing molecular candidates (3,4).

Aim of this communication is to provide an overview of the most recent results obtained by our group in the development of potential spin qubits, in their multitechnique investigation through alternate current susceptometry and pulsed electron paramagnetic resonance spectroscopy, and in the identification and understanding of the molecular parameters which affect the spin dynamics. In this context, three recently reported systems will be presented and discussed.

The investigation of the quantum coherence and the magnetization dynamics of vanadyl phthalocyanine, VOPc, an easily-processable semiconducting molecular material in its pure form, and its crystalline dispersions in the isostructural diamagnetic host TiOPc at different percentages, VOPc:TiOPc 1:10, and VOPc:TiOPc 1:1000, allowed coherent spin manipulation at room-temperature (5).

A comparative study of two vanadium(IV) based systems in which the introduction of a unique structural difference, i.e. an oxovanadium(IV) in a square pyramidal versus a vanadium(IV) in an octahedral environment featuring the same coordinating ligand, allowed to identify in electronic and vibrational features of the vanadyl moiety the source of the enhancement of quantum coherence up to room temperature (6).

Finally, a detailed investigation of the magnetization dynamics by ac susceptometry of a vanadyl complex with diethyldithiocarbamate ligands, which showed an anomalous and unprecedentedly observed field dependence of the relaxation time, revealed important insights on the role of low energy vibrations, experimentally detected by THz spectroscopy, on the spin dynamics [7].

These fundamental studies represent a step towards the identification of optimized molecular building blocks for the preparation of more complex molecular architectures with long-life quantum coherence that can be exploited as molecular quantum gates for quantum computation.

References: 1. M. Warner, S. Din, I. S. Tupitsyn, G. W. Morley, A. M., Stoneham, J. A. Gardener, Z. Wu, A. J. Fisher, S. Heutz, C. W. M. Kay, G. Aeppli, *Nature* **2013**, *503*, 504-508. 2. K. Bader, D. Dengler, S. Lenz, B. Endeward, S.-D. Jiang, P. Neugebauer, J. van Slageren, *Nature Commun.* **2014**, *5*:5304. 3. L. Tesi, E. Lucaccini, I. Cimatti, M. Perfetti, M. Mannini, E. Morra, M. Chiesa, A. Caneschi, L. Sorace, R. Sessoli, *Chem. Sci.* **2016**, *7*, 2074-2083. 4. J. M. Zadrozny, J. Niklas, O. G. Poluektov, D. E. Freedman, *ACS Cent. Sci.* **2015**, *1*, 488-492. 5. M. Atzori, L. Tesi, E. Morra, M. Chiesa, L. Sorace, R. Sessoli, *J. Am. Chem. Soc.* **2016**, *138*, 2154-2157. 6. M. Atzori, E. Morra, L. Tesi, M. Chiesa, L. Sorace, R. Sessoli, *J. Am. Chem. Soc.* **2016**, *138*, 11234-11244. 7. M. Atzori, L. Tesi, S. Benci, A. Lunghi, R. Righini, A. Taschin, R. Torre, L. Sorace, R. Sessoli, *J. Am. Chem. Soc.* **2017**, *139*, 4338-4341.

Olefin Metathesis Ruthenium Catalysts Bearing Backbone-Substituted Unsymmetrical NHC Ligands

Fabia Grisi[a], *Veronica Paradiso*[a], *Chiara Costabile*[a], *Valerio Bertolasi*[b]

[a]*Dipartimento di Chimica e Biologia "Adolfo Zambelli" , Via Giovanni Paolo II, 132, 84084 Fisciano (SA) Italy;* [b]*Dipartimento di Chimica e Centro di Strutturistica Diffrattometrica, Università di Ferrara, Via L. Borsari 46, I-44100 Ferrara, Italy;*
fgrisi@unisa.it

N-heterocyclic carbenes (NHCs) have gained increasingly importance in modern chemistry as excellent ancillary ligands for metal catalysts. Due to their unique steric and electronic properties, efficient catalysts for a huge number of academically and industrially important processes have been found.(1,2) One of the most important and extensively studied transformations mediated by NHC-metal complexes is ruthenium-catalyzed olefin metathesis.(3,4,5) The fine tuning of steric and electronic properties of the NHC ligand can strongly influences catalytic behavior of the resulting ruthenium complexes. In this context, the development of unsymmetrical NHCs (uNHCs), able to differentiate steric bulkiness in proximity of the ruthenium center, has led to important effects on reactivity and selectivity of the resulting catalysts.(6) Recently, we investigated the impact of differently oriented substituents on the backbone of uNHCs as an effective means to modulate the catalytic properties of the resulting complexes.(7,8) The catalytic behavior of new uNHCs combining different backbone configurations with *N*-alkyl/*N*-aryl substituents of variable bulkiness on catalyst properties will be discussed**.**

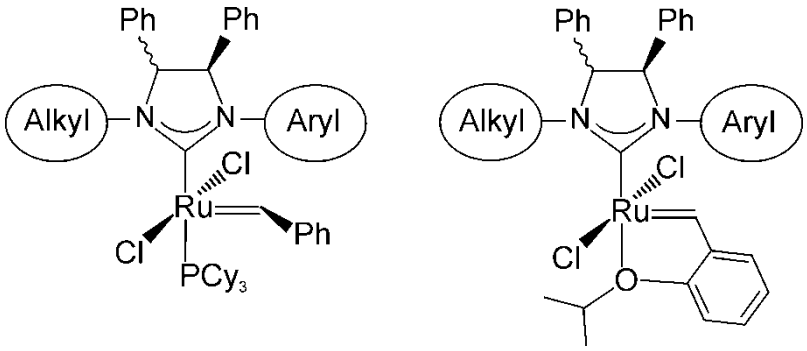


Figure 1. New Grubbs' and Hoveyda-Grubbs' second generation catalysts with uNHCs**.**

References: 1 M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature*, **2014**, *510*, 485. 2. *N-Heterocyclic Carbenes:Effective Tools for Organometallic Synthesis*; ed. S. P. Nolan, Wiley-VCH, 2014. 3. *Olefin Metathesis Theory and Practice*, ed. K. Grela, J. Wiley & Sons: Hoboken, NJ, 2014. 4. G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.*, **2010**, *110*, 1746. 5. C. Samojlowicz, M. Bieniek, K. Grela, *Chem. Rev.*, **2009**, *109*, 3708. 6. F. B. Hamad, T. Sun, S. Xiao, F. Verpoort, *Coord. Chem. Rev.*, **2013**, *257*, 2274. 7. V. Paradiso, V. Bertolasi, F. Grisi, *Organometallics*, **2014**, *33*, 5932. 8. V. Paradiso, V. Bertolasi, C. Costabile, F. Grisi, *Dalton Trans.* **2016**, *45*, 561.

4,4' bipyridine monoxide (bipyMO): a simple heterotopic divergent ligand

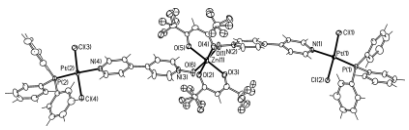
Lidia Armelao[b], Daniela Belli Dell'Amico[a], Gregorio Bottaro[b], Luca Labella[a], Fabio Marchetti[a], Simona Samaritani[a]

[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Giuseppe Moruzzi 13, I-56124; [b] Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1,I-35131; luca.labella@unipi.it

Although 4,4' bipyridine (bipy) can be considered a classical connector since it has been used to prepare a huge number of *d* metal coordination polymers (1) and the oxidized 4,4' bipyridine dioxide (bipyDO) has been largely chosen to prepare examples with the oxophilic lanthanides (2), 4,4' bipyridine monoxide (bipyMO) has been mostly neglected and only a few examples of metal complexes have been reported so far. In most of them bipyMO is coordinated as a terminal ligand through the nitrogen or the oxygen donor atom in dependence of the nature of the metal (3) while only rarely bipyMO is a divergent ligand acting as a bridge in homo-metallic derivatives. (4) Examples where the ligand bridges two different metals are missing in the literature.

In this contribution, a few homo and hetero-metallic complexes of bipyMO for *d* and *f* transition metals are reported. Isostructural homo-metallic coordination polymers $[M(hfac)_2(bipyMO)]_n$ (M = Zn, Cu, Co, Mn; hfac = hexafluoroacetylacetonate) have been prepared. Every bipyMO ligand bridges two metal centers forming a monodimensional metal-bipyMO network with two different metal coordination polyhedrons, $M(hfac)_2N_2$ and $M(hfac)_2O_2$. In the former two bipyMO ligands are coordinated through their N-donor atoms while in the latter through their O-donor atoms. Such a result opened the way to the synthesis of hetero-bimetallic chains with exactly alternated metal centres showing a sufficiently different affinity for nitrogen and oxygen donor ligands. Monodimensional coordination polymers alternating either two different *d* transition ions, $[Mn(hfac)_2(bipyMO)Cu(hfac)_2(bipyMO)]_n$ or *d* and *f* transition metals $[M(hfac)_2(bipyMO)Ln(hfac)_3(bipyMO)]_n$, where M/Ln are Cu/Eu, Zn/Eu, or Co/Dy, were prepared and structurally characterized. Luminescence studies on the europium containing samples have been carried out.

Molecular compounds containing the terminal ipodentate ligand have been obtained for metals showing a high preference between the two donor atoms. A mononuclear platinum complex *cis*-$PtCl_2(PPh_3)$(bipyMO) where the ligand is bonded through the nitrogen atom and the dinuclear $[Eu_2(hfac)_6(\mu\text{-bipyMO})_3]$ where the ligand is bonded through the oxygen atom have been structurally characterized. These complexes can behave as ligands as exemplified by the synthesis of the trinuclear [*trans*-$PtCl_2PPh_3$bipyMO]$_2$Zn$(hfac)_2$.



References:
1. K. Biradha, M. Sarkar, L. Rajput, Chem. Commun., (2006) 4169.
2. D.L. Long, A.J. Blake, N.R. Champness, C. Wilson, M. Schroder, Chem. Eur. J. 8 (2002) 2026.
3. a) D. J. Hoffart, N. C. Habermehl, S. J. Loeb, Dalton Trans., (2007) 2870; b) V. N. Vukotic, S. J. Loeb, Supramol. Chem., 28 (2016) 151.
4. (a) O. Toma, N. Mercier, M. Bouilland, M. Allain, CrystEngComm., 14 **(**2012) 7844. (b) A. A. Dar, G. A. Bhat, R. Murugavel, Inorg. Chem., 55 (2016) 5180. (c) O. Toma, N. Mercier, M. Allain, F. Meinardi, C. Botta, Eur. J. Inorg. Chem., (2017) 844.

Catalysis by Group IV Amido-Pyridinate Complexes for the Reduction of Carbon Dioxide to Methane

L. Luconi,[a] G. Tuci,[a] A. Rossin [a] and G. Giambastiani [a]

[a] Institute of Chemistry of Organometallic Compounds - ICCOM-CNR, Via Madonna del Piano, 10 50019, Sesto F.no, (Fi), Italy. Email: lapo.luconi@iccom.cnr.it

A highly attractive renewable energy technology involves the transformation of CO_2 into fuel. Indeed, CO_2 has not to be regarded as a waste product from the combustion of fossil fuel but rather as a chemical resource to be harvested and recycled into products of added value using the assistance of a catalyst. The metal-mediated CO_2 reduction with silanes (hydrosilylation) is a thermodynamically favored chemical process and it can be conveniently applied to the transformation of this feedstock.

Early transition-metal complexes stabilized by nitrogen-containing ligands have been identified as valuable candidates for a number of highly efficient and selective catalytic transformations (1). In particular, amidopyridinate Group-IV organometallics have shown excellent performance as catalysts precursors in olefins oligomerization, polymerization, and copolymerization (1,2) as well as in the intramolecular hydroamination of primary and secondary aminoalkenes (3).

In search for catalytic applications in the renewable energy field, we have focused on a new class of neutral dibenzyl Zr^{IV} and Hf^{IV} complexes stabilized by a tridentate dianionic benzoimidazolyl-amidopyridinate ligand [$(N^-,N,N^-)M^{IV}Bn_2$; M = Zr, Hf] as pre-catalysts for the CO_2 hydrosylilation reaction.(4) In this study, we have demonstrated that their *in-situ* activation with an equimolar amount of $B(C_6F_5)_3$ leads to the generation of cationic monoalkyl species (Figure 1). In the presence of silanes, these cations promote the CO_2 reduction to methane under mild reaction conditions (room temperature and 1 atm of CO_2). ^{13}C- and $^{13}C\{^1H\}$-NMR experiments with isotopically enriched $^{13}CO_2$ have been conducted to check the reaction course through the generation and conversion of all the reduction intermediates. A full account of the catalytic performance of these Group IV amido-pyridinate complexes in the reduction of carbon dioxide with various hydrosilanes will be discussed.

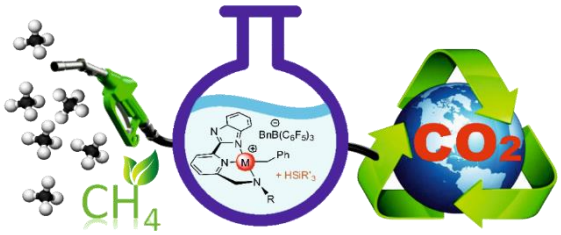


Figure 1. CO_2 reduction to methane catalyzed by cationic $(N^-,N,N^-)M^{IV}Bn$ (M = Zr, Hf) complexes in presence of hydrosilanes.

Acknowledgment. PRIN 2015 Project SMARTNESS (2015K7FZLH) "Solar driven chemistry: new materials for photo- and electro-catalysis" and the bilateral CNR-RFBR Project 2015-2017 (Italy-Russian Federation) are acknowledged for funding this research activity.

References:

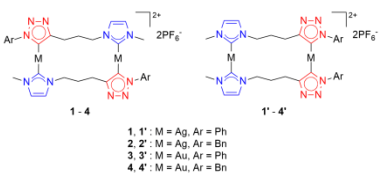
1. a) G. Giambastiani, L. Luconi, R. L. Kuhlman, P. D. Hustad, in *Olefin Upgrading Catalysis by Nitrogen-based Metal Complexes I* , vol. 35, Springer Ed., **2011**, pp. 197-279; b) L. Luconi, A. Rossin, G. Tuci, I. Tritto, L. Boggioni, J. J. Klosin; C. N. Theriault, G. Giambastiani, *Chem. Eur. J.* **2012**, *18*, 671; c) L. Luconi, A. Rossin, G. Tuci, S. Germain, E. Schulz, J. Hannedouche, G. Giambastiani, *ChemCatChem* **2013**, *5*, 1142; d) L. Luconi, A. Rossin, A. Motta, G, Giambastiani, *Chem. Eur. J.* **2013**, *19*, 4906; e) L. Luconi, J. Klosin, A. J. Smith, S. Germain, E. Shulz, J. Hannedouche, G. Giambastiani, *Dalton. Trans.* **2013**, *42*, 16056.
2. L. Luconi, G. Giambastiani, A. Rossin, C. Bianchini, A. Lledos, *Inorg. Chem.* **2010**, *49*, 6811.
3. D. M. Lyubov, L. Luconi, A. Rossin, G. Tuci, A. V. Chercasov, G. K. Fukin, G. Giambastiani, A. A. Trifonov, *Chem. Eur. J.* **2014**, *20*, 3487.
4. L. Luconi, G. Giambastiani, *unpublished results.*

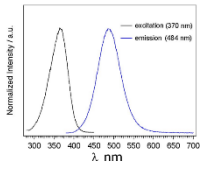
Dinuclear d^{10} complexes with *n*NHC/*tz*NHC heteroditopic carbene ligands and their luminescence properties

Marco Monticelli[a,b], Marco Baron[a], Andrea Longhi[a], Cristina Tubaro[a], Stéphane Bellemin-Laponnaz[b], Claudia Graiff[c], Marzio Rancan[d], Gregorio Bottaro[d], Lidia Armelao[a,d]

[a] Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy;
[b] Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg-CNRS UMR 7504, 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France;
[c] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università degli Studi di Parma, Parco Area delle scienze 17/A, 43124 Parma, Italy;
[d] Institute of Condensed Matter Chemistry and Technologies for Energy (ICMATE), National Research Council (CNR), c/o Department of Chemistry, University of Padova, via Marzolo 1, 35131 Padova, Italy.
marco.baron@unipd.it

Homoleptic gold complexes with N-heterocyclic carbene (NHC) ligands are nowadays studied for a multitude of applications.(1) This type of organometallic complexes, in which all the coordination sites on the gold center are occupied by carbene donors, are characterized by a high stability, due to the strength and inertness of the gold-NHC bond, which can be further enhanced by using multidentate NHC ligands.(2) As a consequence, this family of compounds is scarcely appealing for catalytic applications but earns success in other areas such as luminescent materials,(3) medicinal chemistry,(4) and more recently also molecular recognition and sensing.(5) We are interested since few years in the study of the luminescence properties of dinuclear gold(I) diNHC complexes of general formula $[Au_2(\mu\text{-diNHC})_2](PF_6)_2$. The photoemission in these systems arises from the so-called "aurophilicity", a dispersive interaction between the gold centers, whose presence is usually accompanied by high quality emission.(3) Our efforts to understand the different factors affecting the luminescence properties of the complexes have been focused up to now in modifying the bridging group between the carbene units. We identified the trimethylene group ($-CH_2CH_2CH_2-$) as a privileged linker because it presents the right length and flexibility for allowing the interaction between the two gold centers. In this contribution, we present our recent results on the study of asymmetric bidentate ligands bearing a *n*NHC (*normal* N-heterocyclic carbene) and a *tz*NHC (*1,2,3-triazole* N-heterocyclic carbene) linked by a trimethylene bridge. Synthesis, structural characterization and emission properties of the novel gold(I) complexes will be presented and compared to those of the corresponding silver(I) complexes. Preliminary results on the synthesis of heterobimetallic Ag(I)/Au(I) complexes with this type of ligands will be also illustrated.





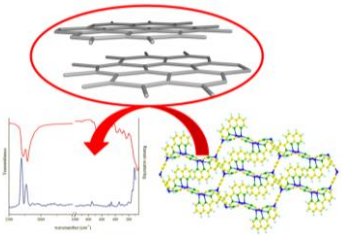
3 - solid state

References:
1. L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903–1912.
2. A. Biffis, M. Baron, C. Tubaro, *Adv. Organomet. Chem.* **2015**, *63*, 203-288.
3. M. Baron, C. Tubaro, A. Biffis, M. Basato, C. Graiff, A. Poater, L. Cavallo, N. Armaroli, G. Accorsi, *Inorg. Chem.* **2012**, *51*, 1778−1784.
4. B. Bertrand, A. Casini, *Dalton Trans.* **2014**, *43*, 4209–4219.
5. J. K.-H. Wong, M. H. Todd, P. J. Rutledge, *Molecules* **2017**, *22*, 200.

Symbiotic structural and spectroscopic approach to reticular chemistry: the case study of luminescent Copper(I) cyanide coordination polymers.

Eliano Diana[a], *Emanuele Priola*[a], *Francesca Grifasi*[a], *Roberto Gobetto*[a], *Michele R. Chierotti*[a],

[a]*Università di Torino, Via Pietro Giuria 7, elino.diana@unito.it*



The reticular description of coordination polymers in recent years attracted a great interest for its easiness and compactness. (1) The use of the graph formalism to characterize complex structures by considering only the connection between nodes and a simplified description of the non-bridging fragments is a powerful tool both in a predictive and a comparative point of view. (2) However, this theory has usually been limited only to the structure description, without considering the effect of net structure on the spectroscopic behavior of the different materials. The connection of topological invariants typical of a specific family of coordination polymers with some characteristics NMR or vibrational pattern could be useful when is difficult to obtain single crystals, and can be a powerful aid to the structure resolution by means of powder X-ray diffraction of complex structures. However, this correlation is often not so clear: spectra signals of complex molecules usually don't reflect the long range spatial disposition, but only the local environment, that is only partially correlated to the overall topology. In other cases, the coupling between signals, especially in the case of simple bridging molecules, is very informative. This is the case of cyanide; this bridging anion has a prominent role in the reticular chemistry, and despite the common simple linear coordination geometry, demonstrated to be a powerful tecton to construct a multitude of different coordination polymer topologies, by choosing different metal nodes. (3) An interesting system is done by the copper (I) cyanide: the non-obvious preference of copper (I) for a specific coordination geometry and the different bridging possibilities shown by the cyanide ligand, make very difficult to predict the reticular chemistry of copper cyanide coordination polymers, that possess a peculiar emissive behavior that make these systems interesting for LED applications and sensoristics. (4) We reported the synthesis and characterization of 12 new compounds of copper cyanide with different geometries and arrangements of the ligands, with very different topologies. These topologies are connected by the presence of some typical topological invariants build up by cyanide and metal centers, like rings of different dimensions and chains. After a comment on the possibility to control the topology of the compound by a judicious choice of the ligand and by a different synthetic approach, it will be analyzed the correlation of vibrational and NMR analysis and the topological connectivity of the specific fragments, demonstrating that in some cases this correlation can be rationalized.

References:

1. V.A. Blatov, A.P. Shevchenko, D.M. Proserpio, Cryst. Growth Des. 2014, 14, 3576-3586.
2. M. O'Keeffe, O.M. Yaghi, Chem. Rev. 2012, 112, 675-702.
3. E.V. Alexandrov, A.V. Virovets, V.A. Blatov, E.V. Peresypkina, Chem. Rev. 2015, 115, 12286–12319
4. A.N. Ley, L.E. Dunaway, T.P. Brewster, M.D. Dembo, T.D. Harris, F. Baril-Robert, X. Li, H.H. Patterson, R.D. Pike, Chem Commun., Chem.Commun. 2010,46, 4565–4567.

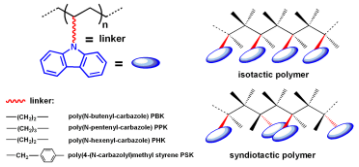
Polymer Stereoregularity Influence on Optical Properties of Carbazole-based Photoconductor Polymers

Stefania Pragliola [a], *Antonio Botta* [a], *Vincenzo Venditto* [a], *Amalia Velardo* [a], *Rosalba Liguori* [b], *Alfredo Rubino* [b]

[a] *Department of Chemistry and Biology (DCB) and INSTM Research Unit, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy;* [b] *Department of Industrial Engineering (DIIn), University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy; E-mail: spragliola@unisa.it*

Carbazole-based compounds have gained in importance in the last few decades because of their use as organic photoconductor, photorefractive and light-emitting materials etc.(1). From the structural point of view, carbazole containing polymers can be divided into two groups: polymers with in-chain isolated carbazole groups and polymers with pendant carbazole groups, like poly(N-vinylcarbazole) (PVK) the first to be synthesized. Despite its low electrical conductivity, PVK has been largely used in combination with other layers in the fabrication of organic light emitting diodes (OLEDs) (1). As for the PVK homologues, it is generally accepted that photoconductivity is affected by the chemical nature of the spacer linking the carbazole chromophore to the main chain as well as the stereochemical configuration of the polymer chain.(1-5).

In this contribution, the synthesis and physical properties of stereoregular poly(carbazole)s presenting different spacers linking pendant carbazole groups to the polymer main chain are reported.



Polymerizations were performed by using homogeneous Ziegler-Natta catalytic systems. Polymers have been fully characterized by NMR, X-ray diffraction, thermal analysis, FT-IR and UV-Vis as well as photoluminescence analysis. Moreover, the influence of the polymer stereoregularity on the optical properties of achieved poly(carbazole)s has been also investigated. The optical analysis of all polymer film samples reveals the presence of two different excimers arising from a fully ("sandwich-like", low energy excimer) or partially (higher energy excimer) overlapping of two carbazole groups. In detail, the isotactic polymers show a higher emission intensity ratio between "sandwich-like" and "partially overlapping" excimers respect to syndiotactic ones. Thin polymer films have been tested as single emissive layers of OLEDs. A blue light is obtained from all the devices, except for the isotactic poly(*N*-pentenylcarbazole)-based OLED with an optimized architecture that emits a white light.

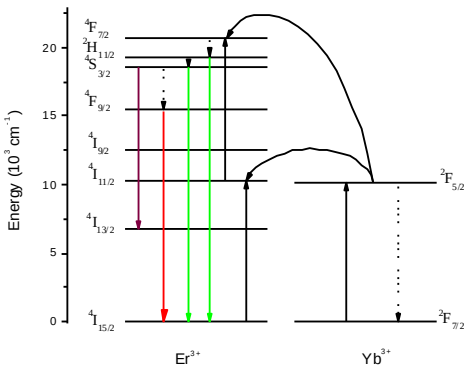
References:
1. J.V. Grazulevicius, P. Strohriegl, J. Pielichowski and K. Pielichowski, Prog. Polym. Sci. 28 (2003) 1297-1353.
2. A. Botta, S. Pragliola, V. Venditto, A. Rubino, S. Aprano, A. Del Mauro De Girolamo, M.G. Maglione, C. Minarini, Polym. Compos. 36 (2015) 1110-1117.
3. A. Botta, S. Pragliola, V. Venditto, A. Rubino, S. Aprano, A. Del Mauro De Girolamo, M.G. Maglione, C. Minarini, Times of polymers (TOP) and composites, in: Book Series: AIP Conference Proceedings, 1599 (2014) 493-497.
4. A. Botta, V. Venditto, A. Rubino, S. Pagliola, J. Chem. (2016) 1656459.
5. A. Botta, S. Pragliola, C. Capacchione, A. Rubino, R. Liguori, A. De Girolamo Del Mauro, V. Venditto Eur. Polym. J. 88 (2017) 246-256.

Upconverting polymeric aerogels

Christophe Daniel[a], Paolo Cortelletti[b], Marco Pedroni[b], Gaetano Antonio D'Amora[a], Gaetano Guerra[a], Adolfo Speghini[a]

[a]Department of Chemistry and Biology "A. Zambelli", Università di Salerno and INSTM, RU of Salerno, Via Giovanni Paolo II, 84084 Fisciano, Salerno, Italy
[b]Nanomaterials Research Group, Department of Biotechnology, Università di Verona and INSTM, RU of Verona, Strada le Grazie 15, 37134 Verona, Italy

Aerogels constitute an important class of highly porous materials and their unique properties make them interesting for many technological applications such as thermal and acoustic insulation, catalysts/ catalyst supports, water/air purification and airborne particle filtration.[1]
Upconverting lanthanide doped alkaline-earth fluoride nanoparticles (e.g. SrF_2 or CaF_2 doped with Yb^{3+} and Er^{3+} ions) with typical particle size of 20 nm were prepared by a facile, environmental friendly hydrothermal technique, using oleate group as a capping agent[2].
The nanoparticles (NPs) have been then incorporated in syndiotactic polystyrene (s-PS) aerogels polymer. The monolithic s-PS/NP aerogels with NPs amount up to 50 wt% have been prepared by a sol-gel process followed by solvent extraction with supercritical CO_2. These composite NP/s-PS aerogels are characterized by an apparent porosity up to 98% and surface area up to 300 m^2/g. The SEM analysis have also shown that the aerogels display a fibrillar morphology with the dispersion of NPs within the aerogel macropores.
Spectroscopic properties have been investigated using a 980 nm laser as the excitation source. An evident upconversion emission of the Er^{3+} ions in the visible and near infrared range, in particular in the green and red regions, has been observed and investigated.



Mechanism for the upconversion emission under 980 nm excittion

References:

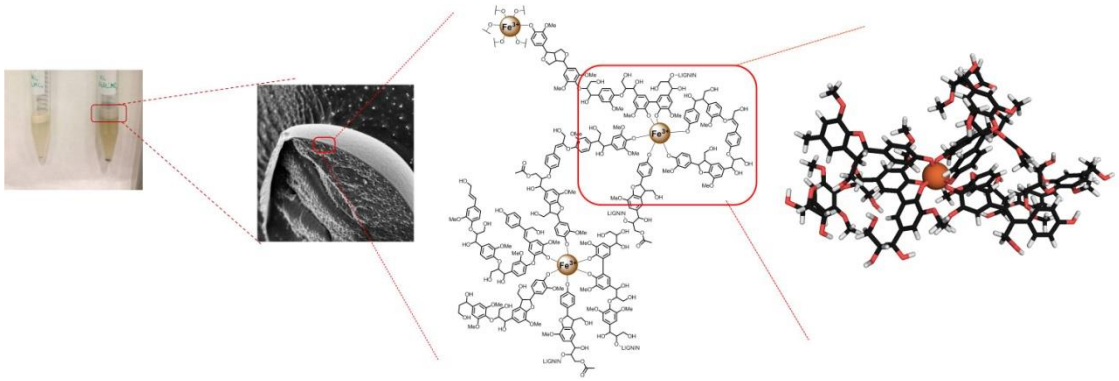
1. Daniel, C.; Longo, S.; Ricciardi, R.; Reverchon, E.; Guerra, G., Monolithic nanoporous crystalline aerogels. *Macromol. Rapid Commun.* **2013,** *34* (15), 1194-207.
2. Pedroni, M.; Piccinelli, F.; Passuello, T.; Giarola, M.; Mariotto, G.; Polizzi, S.; Bettinelli, M.; Speghini, A., Lanthanide doped upconverting colloidal CaF_2 nanoparticles prepared by a single-step hydrothermal method: toward efficient materials with near infrared-to-near infrared upconversion emission. *Nanoscale* **2011,** *3* (4), 1456-1460.

Coordination Complexes and One Step Assembly of Natural Polyphenols for Versatile Nanocapsule Engineering

C. Crestini, H. Lang, L. Zongo

University of Rome Tor Vergata, Department of Chemical Sciences and Technologies, Via della Ricerca Scientifica, 00133 Rome, Italy
e-mail: crestini@stc.uniroma2.it

Nanoencapsulation of active substances with controlled release in harmless matrices has been the subject of numerous scientific efforts mainly due to the significant biomedical potential of such endeavors. Lignin, the environmentally sustainable by-product of the pulp and paper industry, contains a multitude of phenolic hydroxyl groups, some of which, are known to readily and strongly chelate with iron ions. In this effort we demonstrated that the concerted use of chelation chemistry, oil in water emulsion principles and low energy sonication, offers a facile, one pot strategy to assemble lignin nanocapsules (LNCs) of a controlled architecture. Under these conditions capsules are shown to rapidly assemble utilizing two driving forces, the π-stacking propensity of lignin and its metal chelating ability at alkaline pH. Detailed size exclusion chromatographic evidence validates that the formation of capsules is driven mainly by the enumerated physical interactions with no significant chemical modification of the lignin. The developed process was systematically optimized so as to create the foundations for the morphology and the yield of the capsules being modulated as a function of sonication time, power and surface contact area. Both pure LNCs and Fe-LNCs were synthesized in high yields with size distributions varying from 0.3 to 5 μm and their release efficiencies evaluated in detail. As anticipated, the complexation effects of the phenolic OH groups offered to the Fe-LNCs, increased stability, reduced shell thickness (allowing for greater loading efficiencies) and lower release kinetics, compared to LNCs.



References

1. Tortora, M.; Cavalieri, F.; Mosesso, P.; Ciaffardini, F.; Melone, F.; Crestini, C. *Biomacromolecules* **2014**, *15* (5), 1634–1643.
2. Bartzoka, E.D. Lange, H Thiel, K. Crestini C. *ACS Sustainable Chem. Eng.*, Just Accepted Manuscript • DOI: 10.1021/ acssuschemeng.6b00904 • Publication Date (Web): 13 Jun **2016**

Acknowledgements: This work was funded by theEU-funded research project 'New bio-inspired processes and products from renewable feedstocks – BIO-MIMETIC' (grant agreement No. 282945).

Mesoporous bioactive glasses doped with cerium: investigation of catalase and SOD mimetic activities, and bioactivity

Valentina Nicolini[a], Gianluca Malavasi[a], Ledi Menabue[a], Gigliola Lusvardi[a], Francesco Benedetti[b,c], Sergio Valeri[b,c], Paola Luches[c]

[a] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via Campi 103, 41125 Modena, Italy; [b] Department of Physics, Informatics and Mathematics, University of Modena and Reggio Emilia, via Campi 213/a, 41125 Modena, Italy; [c] Istituto Nanoscienze-CNR, via Campi 213/a, 41125 Modena.

We investigate the ability of mesoporous bioactive glasses doped with cerium ions (Ce^{3+}/Ce^{4+}) to act as catalase and superoxide dismutase (SOD) mimic materials. Our aim is to synthesize a material able to show both bioactivity and antioxidant properties. Bioactive Ce-doped glasses synthesized via melting technique (molten glasses) have shown good catalytic properties, but low bioactivity (formation of hydroxyapatite); thus we decided to modify with cerium oxide a class of glasses that has already demonstrated to have better bioactivity properties than the classical molten glasses. This class is constituted of mesoporous bioactive glasses synthesized through the EISA (Evaporation-Induced Self-Assembly) method and have a very high surface area. Because of this, their reactivity is increased with respect to the molten glasses, and they show the formation of hydroxyapatite over the surface at a shorter times as compared to the molten bioactive glass 45S5 Bioglass®. The XPS data collected in previous studies on the valence state of cerium in the molten bioactive glasses highlighted that on the surface of the samples there were both Ce^{3+} and Ce^{4+} ions and that during the catalase tests their ratio changed (1-3) as it happens in nanoceria. (4) Moreover, the Ce^{3+}/Ce^{4+} ratio on the glass surface was shown to depend on the glass composition: the presence of phosphate in the molten bioactive composition favors the increase of Ce^{3+} amount and in the same time decrease of the catalase mimetic activity.

Starting from this state of the art, we have decided to study Ce-mesoporous glasses: i) with different compositions in order to verify how the glass composition affects the catalase-like activity; ii) with both good bioactivity and good antioxidant properties. We have tested the SOD and the catalase mimic activities on glasses with different Ce^{3+}/Ce^{4+} ratio (range 3.9-0.7) in order to find the better synthesis conditions.

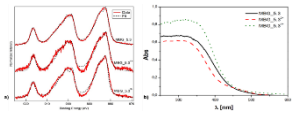


Figure: a) Ce 3d XPS spectra of the MBG_5.3, MBG_5.3^{3+}, and MBG_5.3^{4+} as prepared powders compared with the b) UV-Vis spectra performed over the same samples.

The catalase and SOD mimic activity tests have revealed that the Ce-mesoporous glasses are able to act as mimic materials for the two enzymes. In addition, the FT-IR and XRD analysis have confirmed that in several samples the hydroxyapatite is present, even if, increasing the content of cerium oxide, the intensity of the characteristic peaks of hydroxyapatite decreases. These results highlight that it is possible to obtain a glass with both antioxidant properties and bioactivity.

References: 1. V. Nicolini, E. Gambuzzi, G. Malavasi, L. Menabue, M.C. Menziani, G. Lusvardi, A. Pedone, F. Benedetti, P. Luches, S. D'Addato, S. Valeri, Evidence of Catalase Mimetic Activity in Ce 3+ /Ce 4+ Doped Bioactive Glasses, J. Phys. Chem. B. 119 (2015) 4009–4019. 2. V. Nicolini, E. Varini, G. Malavasi, L. Menabue, M.C. Menziani, G. Lusvardi, A. Pedone, F. Benedetti, P. Luches, The effect of composition on structural, thermal, redox and bioactive properties of Ce-containing glasses, Mater. Des. 97 (2016) 73–85. 3. V. Nicolini, G. Malavasi, L. Menabue, G. Lusvardi, F. Benedetti, S. Valeri, P. Luches, Cerium-doped bioactive 45S5 glasses: spectroscopic, redox, bioactivity and biocatalytic properties, J Mater Sci (2017). doi:10.1007/s10853-017-0867-2. 4. T. Pirmohamed, J.M. Dowding, S. Singh, B. Wasserman, E. Heckert, A.S. Karakoti, J.E.S. King, S. Seal, W.T. Self, Nanoceria exhibit redox state-dependent catalase mimetic activity, Chem. Commun. 46 (2010) 2736.

Tetrahedral Arrays of Metallo-porphyrins

[a]Marianna Marchini, [b]Alessandra Luisa, [a]Giacomo Bergamini, [c]Nicola Demitri, [a]Massimo Baroncini, [a]Paola Ceroni, [b]Elisabetta Iengo

[a] Department of Chemistry "G.Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy
[b] Dep. Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy; [c] Elettra – Sincrotrone Trieste, S.S. 14 Km 163.5 in Area Science Park, 34149 Basovizza Trieste, Italy.
E-mail: marianna.marchini2@unibo.it

Artificial photosystems mimicking the natural occurring ones (1) play a prominent role in the contemporary research (2). In particular, the study of multichromophoric systems with a shape-persistent arrangement of the chromophores has gained increasing relevance since new properties may emerge from the interaction between the spatially organized units. In this context, we studied a supramolecular system constituted by four ruthenium porphyrins and a tetramer based on pyridylpyridium units.

The ruthenium porphyrin was synthetized in Prof. Elisabetta Iengo's group (University of Trieste), whereas the pyridylipyridium derivates (3) were synthetized in our laboratory in Bologna.

By NMR and spectrophotometric experiments it was possible to estimate the stoichiometry of the supramolecular complex: 1:1 in the case of pyridylipyridium monomer model and 1:4 for the tetramer.

The tetramer is a good water-soluble chromophore (40% quantum yield), and we were able to follow the complexation also by looking at the changes in the tetramer fluorescence and porphyrin phosphorescence. The final complex, in fact, is not emissive because of the formation of a low lying charge transfer state.

The crystal structures of the complexes have been fully resolved by X-ray measurements performed at the ELETTRA Synchrotron in Trieste.

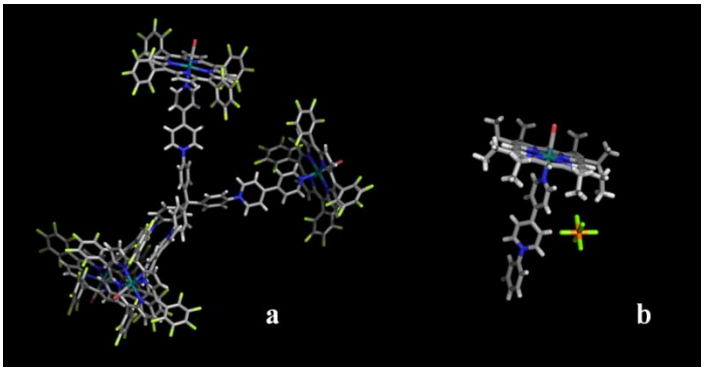


Figure 8 Crystal structure of ruthenium porphyrins-tetramer array (a) and ruthenium porphyrin-monomer array (b).

References:
1. "Electron Transfer in Chemistry" Balzani, V., Ed.; Wiley-VCH: Weinheim (Germany) 2001: Gust, D. et al. Vol. III, Part 2, Chapter 2, pp 273−336 and Fukuzumi, S. et al. Vol. II, Part 2, Chapter 8, pp 927−966.
2. Scholes, G. D.; Fleming, G. R.; Olaya-Castro, A.; van Grondelle, R. Nat. Chem., 2011, 3, 763.
3. Bergamini, G.; Fermi, A.; Marchini, M.; Locritani, M.; Credi, A.; Venturi, M.; Negri, F.; Ceroni, P.; Baroncini, M. Chem. Eur. J., 2014, 20, 7054.

Plasmonics Applied to a Nanotheranostic System: Synthesis, Photophysical Properties and Anticancer Activity of Silica/Gold Nanoparticles

Massimo La Deda[a,d], Lucie Sancey[b], Giovanna Palermo[c], Roberto Termine[d], Antonio De Luca[c,d], Elisabeta I. Szerb[e], Iolinda Aiello[a,d], Angela Candreva[a], Loredana Ricciardi[d], Mauro Ghedini[a,d]

[a]Department of Chemistry and Chemical Technology, University of Calabria, 87036 Rende (CS), Italy; [b]IAB U1209 UMR5309 UGA, Université Grenoble Alpes, 38042 Grenoble, France; [c]Department of Physics, University of Calabria, 87036 Rende (CS), Italy; [d]CNR NANOTEC- Institute of Nanotechnology U.O.S. Cosenza, 87036 Rende (CS), Italy; [e]Institute of Chemistry Timisoara of Romanian Academy, 300223, Timisoara, Romania; massimo.ladeda@unical.it

Gold-silica nanoparticles (**Ir_1-$AuSiO_2$**) embedding a luminescent water soluble cyclometalated Ir(III) compound, **Ir_1**, with formula $[(ppy)_2Ir(en)]CH_3COO$ (where ppy= 2-phenylpyridine and en= ethylenediamine), were synthesized (1,2) and used to promote photodynamic and photothermal action on human glioblastoma cells (U87MG). Multifunctionality of this system is the result of three contributes: i) the heavy atom promotes, through excited triplet state formation, an energy transfer process towards molecular oxygen, with generation of $^1O_2$, that is responsible for *the photodynamic effect*; ii) the overlap of the Ir(III) complex emission with gold plasmonic band (3), that allows an energy transfer towards the nanoparticles metallic core, increasing the *photothermal effect*; iii) the photophysical peculiarities of the Ir(III) complex, allowing an excellent emission simultaneously to the transfer processes, make the system an excellent *luminescent bioprobe*. Obtained results were compared with those of nanoparticles synthesized without gold core (**Ir_1-SiO_2**): *in-vitro* cell assays show a good cytotoxic effect and, when observed by confocal fluorescent microscope, an optimal resolution of this nanostructured material into cells, demonstrating that the presented approach can be successfully used in fluorescence imaging as well as a very promising biocompatible platform for the photogeneration of singlet oxygen and photothermal catalysis, achieving an all-in-one nanotheranostic system.

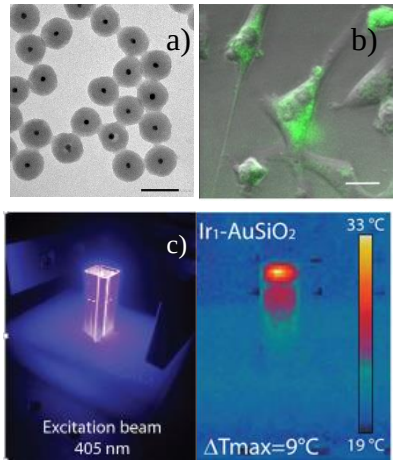


Fig. 1 Ir_1-$AuSiO_2$: a) TEM image; b) confocal image; c)thermal image

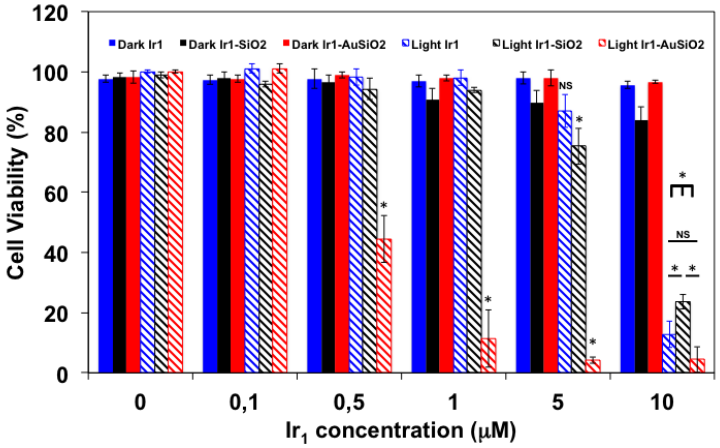


Fig. 2 Dark cytotoxicity and photo-activity of **Ir_1** compared with **Ir_1-SiO_2** and **Ir_1-$AuSiO_2$**. The concentration zero indicates the results for control conditions, in absence of nanoparticles, with or without light exposure.

References: 1. L. Ricciardi, M. Martini, O. Tillement, L. Sancey, P. Perriat, M. Ghedini, E. I. Szerb, Y. J. Yadav, M. La Deda, *J. Photochem. Photobiol. B* 2014, **140**, 396. 2. L. Ricciardi, T. F. Mastropietro, M. Ghedini, M. La Deda, E. I. Szerb, *J. Organomet. Chem.* 2014, **772-773**, 307. 3. A. De Luca, M. Grzelczak, I. Isabel Pastoriza-Santos, L. M. Liz-Marzán, M. La Deda, M. Striccoli, G. Strangi, *ACS Nano*, 2011, **5**, 5823.

Functionalized triazolylidenes as versatile mesoionic carbenes: metal complexes for catalysis and luminescent materials

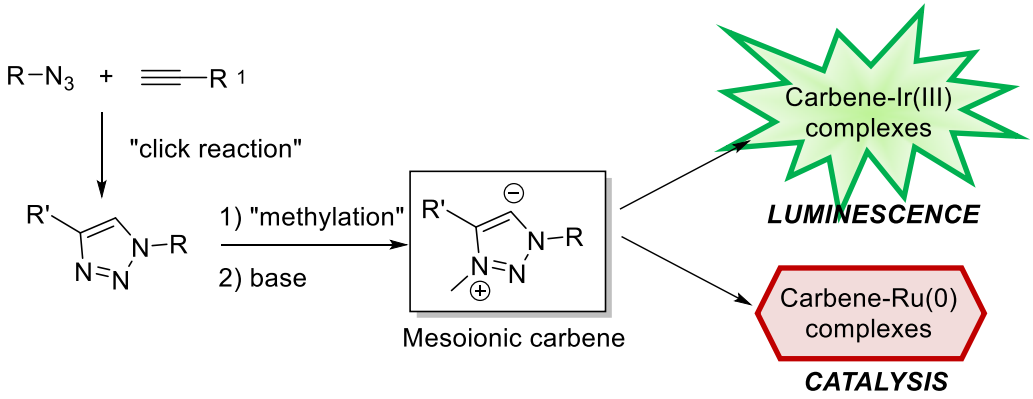
Elia Matteucci[a], Andrea Baschieri[b], Cristiana Cesari[a], Rita Mazzoni[a], Claudia Bizzarri[c] and Letizia Sambri[a]

[a] Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4, I-40136, Bologna, Italy. [b]Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy; [c] Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6 76131 Karlsruhe (D); letizia.sambri@unibo.it

1,2,3-Triazol-5-ylidene derivatives have recently emerged as a new class of so-called mesoionic (MICs) carbenes,(1) and have found a wide range of applications as ligands in metal complexes.(2) The success of this class of ligands is based on a combination of favorable features, as a result of their strong donor character and the easy preparation of the triazole precursors through the regioselective copper(I) catalyzed 'click' cycloaddition of alkynes with azides (CuAAC).(3) Subsequent *N*-alkylation and deprotonation of the readily obtained 1,2,3-triazoles afford the desired mesoionic carbene ligands.(4)

The presence of a heteroatom in a suitable position of a substituent of the triazolilydene can lead to a bis-chelating ligand or to a ligand carrying an activating functionality.

We exploited such triazolylidene mesoionic carbenes to obtain a wide set of both positive and neutral Ir(III)-complexes,(5,6) with good luminescent performances, and neutral Ru(0)-complexes, used as active catalysts in hydrogenation reactions.(6,7)



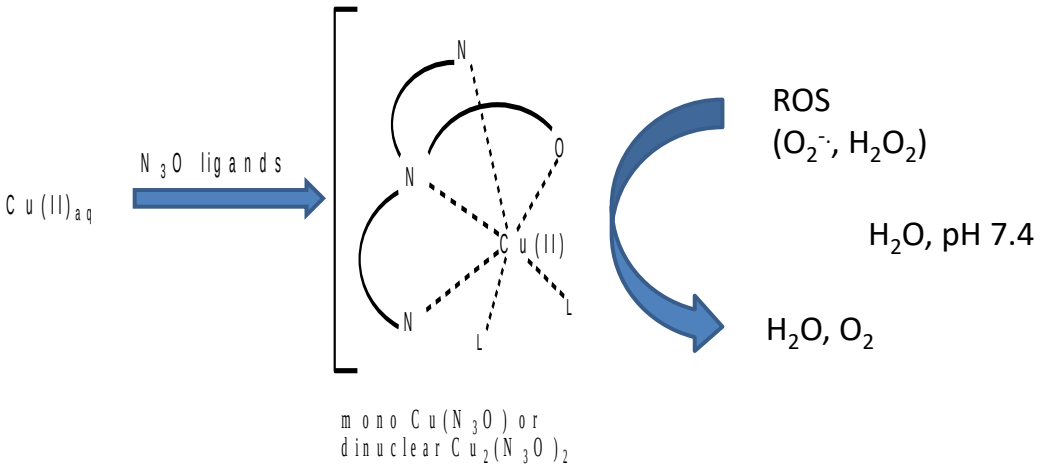
References: 1. a) Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534–13535. b) Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 4759–4762. 2. a) Donnelly, K. F.; Petronilho, A.; Albrecht, M. *Chem. Commun.* **2013**, *49*, 1145–1159.b) Aizpurua, J. M.; Fratila, R. M.; Monasterio, Z.; Pérez-Esnaola, N.; Andreieff, E.; Irastorza, A.; Sagartzazu-Aizpurua, M. *New J. Chem.* **2014**, *38*, 474–480, and cited references. 3. Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599. 4. Crabtree, R. H. *Coord. Chem. Rev.* **2013**, *257*, 755–766 and cited references. 5. A. Baschieri, F. Monti, E. Matteucci, A. Mazzanti, A. Barbieri, N. Armaroli, L. Sambri, *Inorg. Chem.*, **2016**, *55*, 7912-7919. 6. Unpublished results. 7. C. Cesari, A. Cingolani, C. Parise, S. Zacchini, V. Zanotti, M.C. Cassani, R. Mazzoni, *RSC Adv.*, **2015**, *5*, 94707.

Copper complexes with biomimetic antioxidant activity

A. Squarcina, M. Zonzin, M. Carraro, M. Bonchio

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Padova and Istituto per la Tecnologia delle Membrane, ITM-CNR, UOS di Padova, via Marzolo, 1, 35131 Padova, Italy*

The anomalous production of reactive oxygen species (ROS), generated as by-products of normal cellular metabolism, is responsible for an enhanced oxidative stress, which is ultimately associated with several disorders, chronic diseases and ageing. A major defense strategy of living systems against the ROS is represented by the antioxidant enzymes (1). These primarily belong to the superoxide dismutase (SOD) family, whose task is the disproportionation of $O_2^{-\cdot}$ into O_2 and H_2O_2. This latter oxidant is then detoxified by catalase (CAT) enzymes upon conversion into O_2 and H_2O.
The active sites of the antioxidant enzymes contain metal ions as Cu(II) and Mn(III), coordinated by a set of N and O donor atoms. Despite the large availability of metal complexes showing a similar coordination environment, the efficient mimicking of the enzymatic redox activity still represents a challenging goal (2,3).
In this communication, the use of tetradentate N_3O tripodal ligands, for the preparation of antioxidant synthetic enzymes, will be presented. In particular, mononuclear and dinuclear copper complexes have been prepared and tested under physiological-like conditions, in order to assess their structure-dependent catalytic behavior towards SOD-like and CAT-like reactions, showing in some cases an interesting dual activity.



Moreover, since free Cu(II) ions may also be responsible for an enhanced ROS production, the ligands have been tested to scavenge these ions from an aqueous solution, in order to convert their harmful reactivity into a benign antioxidant activity, while the peroxidase-like reactivity of the resulting complexes has been evaluated in the presence of different substrates. The speciation and the stability of the complexes will be also discussed.

1. K. Jomova, M. Valko *Toxicology*, **2011**, *283*, 65-87.
2. A. Squarcina, A. Sorarù, F. Rigodanza, M. Carraro, G. Brancatelli, T. Carofiglio, S. Geremia, V. Larosa, T. Morosinotto, M. Bonchio *ACS Catal.*, **2017**, *7*, 1971–1976.
3. G. Britovsek, M. Grau, F. Rigodanza, A. J P White, A. Sorarù, M. Carraro, M. Bonchio *Chem. Commun.*, **2014**,*50*,4607-4609

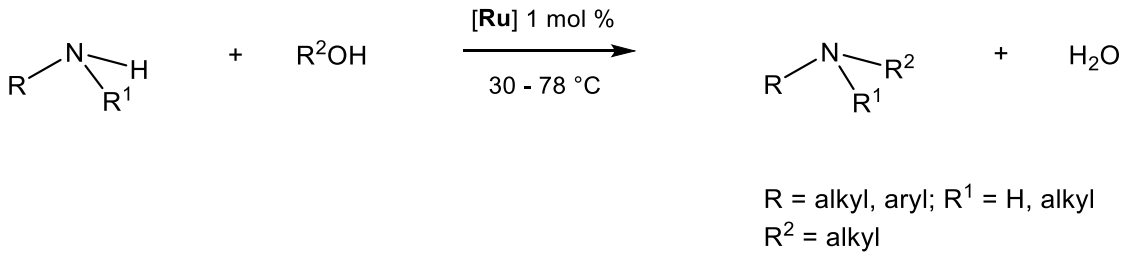
Mild *N*-Alkylation of Amines with Alcohols Catalyzed by Acetate Ruthenium Complexes

Walter Baratta,[a] *Rosario Figliolia*,[a] *Salvatore Baldino*,[a] *Hans Günter Nedden*,[b] *Antonio Zanotti-Gerosa*[b]

[a] *Dipartimento DI4A, Università di Udine, Via Cotonificio 108, 33100 Udine, Italy;* [b] *Johnson Matthey Fine Chemicals Division 28 Cambridge Science Park, Milton Road, Cambridge, CB4 0FP, United Kingdom;E-mail: walter.baratta@uniud.it*

The formation of C-N bonds for the preparation of amines compounds is a reaction of high relevance for the synthesis of bulk and fine chemicals (1). The preparation of several drug molecules involves *N*-substitution transformations that are usually performed by reaction of amines with alkylating agents or via reductive amination. In this context, the catalytic *N*-alkylation of amines using environmentally friendly alcohols as alkylating reagents and affording water as only byproduct, is an attractive atom-economic way for the C-N bond formation (2,3).

We report here the straightforward synthesis of the carboxylate ruthenium complexes of formula $Ru(OAc)_2(diphosphane)(CO)_n$ (n = 0, 1). These compounds are efficient catalysts for the *N*-alkylation of amines using primary alcohols under mild reaction conditions, with an alcohol / amine molar ratio of 10-100. Evidence has been provided that in catalysis a monohydride species is formed through an equilibrium reaction.



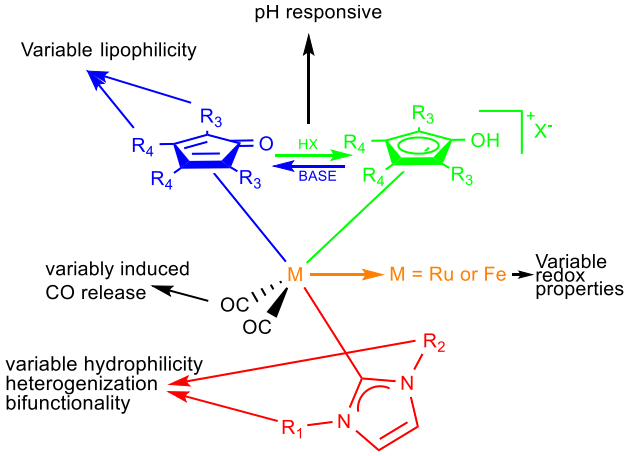
References:
1. J. S. Carey, D. Laffan, C. Thomson, M. T. Williams, *Org. Biomol. Chem.* **2006**, *4*, 2337.
2. X. Ma, C. Su, Q. Xu, *Top. Curr. Chem. (Z)* **2016**, *374*, 27.
3. J. Leonard, A. J. Blacker, S. P. Marsden, M. F. Jones, K. R. Mulholland, R. Newton, *Org. Process Res. Dev.* **2015**, *19*, 1400.

The power of ligand combination in redox active ruthenium and iron complexes.

Rita Mazzoni[a], *Cristiana Cesari*[a], *Andrea Cingolani*[a], *Valerio Zanotti*[a], *Fabrizio Cavani*[a], *Francesco Puzzo*[a], *Carlo Lucarelli*[b], *Massimo Mella*[b], *Andrea Tagliabue*[b], *Tom Baker*[c]

[a] *Dipartimento di Chimica Industriale "Toso Montanari" viale Risorgimento, 4 40136, Bologna"*; [b] *Dipartimento di Scienza e Alta Tecnologia – Università dell'Insubria-Como*; [c] *Department of Chemistry, University of Ottawa, Canada; E-mail rita.mazzoni@unibo.it*

In recent years, cyclopentadienone complexes have drawn attention due to their air-water stability, availability from cheap starting materials, and unique catalytic features arising from the presence of a non-innocent ligand.(1) In the meantime N-heterocyclic carbenes increased their ubiquity as ancillary ligands in catalysis and other fields due to their great potential for both easy synthesis and functionalization.(2) Our recent research interest has been thus devoted to the development of novel ruthenium and iron based complexes combining carbonyls, cyclopentadienones and variously functionalized N-heterocyclic carbenes.(3) These complexes can be rapidly protonated on cyclopentadienone by strong acid (e.g. HOTf) giving rise, in the case of ruthenium, to active precursors for bifunctional hydrogenation and dehydrogenation catalysis.(4)



The straightforward synthetic method allowed the design of complexes containing hydroxyl, amino and pyridine functionalized NHC directed to the improvement of their catalytic activity, to the development of supported materials and to the preparation of water-soluble complexes. Herein, we report on the chemistry of the ruthenium complexes as bifunctional catalysts in hydrogenation and dehydrogenation with particular emphasis on the peculiar role that a basic nitrogen on the lateral chain of NHC can play on the mechanism investigated by *in situ* IR and DFT calculations. Joy and pain of the shift to earth abundant iron congeners will be then described. Finally the potential of these ligand-metal combinations in biphasic catalysis, bio-derived substrate transformations, electrochemistry and bio-inorganic chemistry will be also outlined.

References: 1. A. Quintard and J. Rodriguez Angew. Chem. Int. Ed. 53 (2014), 4044. 2. Hopkinson, M.N., Richter, C., Schedler, M. and Glorius, F., Nature 510 (2014) 485 3. [Ru] C. Cesari, S. Conti, S. Zacchini, V. Zanotti, M. C. Cassani and R. Mazzoni, Dalton Trans., 2014, 43, 17240. [Fe] A. Cingolani, C. Cesari, S. Zacchini, V. Zanotti, M.C. Cassani and R. Mazzoni Dalton Trans., 44 (2015), 19063; 4. Cesari, C., Mazzoni, R., Muller-Bunz, H. and Albrecht, M., J. Organomet. Chem 793 (2015) 256; Cesari, C., Cingolani, A., Parise, C., Zacchini, S., Zanotti, V., Cassani, M.C. and Mazzoni, R., RSC Adv. 5 (2015) 94707.

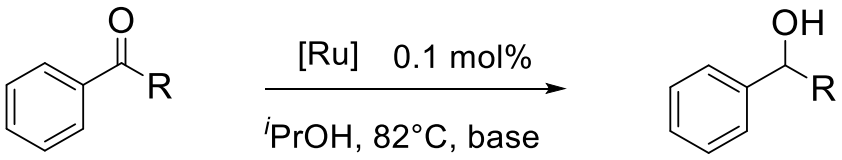
Synthesis of New Carbonyl Diphosphane Ruthenium Complexes for Catalytic C-H Bond Activation Reactions

Rosario Figliolia,[a] *Salvatore Baldino*,[a] *Walter Baratta*,[a] *Steven Gibolout*,[a,b] *Hans Günter Nedden*,[b] *Antonio Zanotti-Gerosa*[b]

[a] *Dipartimento DI4A, Università di Udine, Via Cotonificio 108, 33100 Udine, Italy;* [b] *Johnson Matthey Fine Chemicals Division 28 Cambridge Science Park, Milton Road, Cambridge, CB4 0FP, United Kingdom; E-mail: figliolia.rosario@spes.uniud.it*

Homogeneous catalysis plays a key role in development of new chemo- and enantio-selective syntheses that point to efficiency and low environmental impact. For this purpose, great concern has been devoted to processes that employ non-toxic reagents / solvents and that can be carried out under mild reaction conditions, using low quantities of catalysts. As regards the reduction of carbonyl compounds, ketones and aldehydes are generally converted to alcohols with strongly reducing agents, namely $NaBH_4$ and $LiAlH_4$[(1)]. In addition, dihydrogen at high pressure (HY) has been widely used with ruthenium based catalysts[(2)]. Milder reaction conditions associated with low risks can be achieved via transfer hydrogenation (TH) using 2-propanol catalyzed by efficient ruthenium catalysts[(3)].

We report here a straightforward procedure for the preparation of a class of ruthenium carbonyl compounds $RuX_2(PP)(CO)_n$ (X = Cl, $OCOCH_3$, $OCOCF_3$) (n = 0 - 2) bearing aryl and alkyl diphosphane ligands. Ruthenium hydride complexes are formed by reaction with H_2 via dihydrogen splitting or with hydrogen donor molecules. These derivatives easily react with nitrogen ligands affording efficient catalytic species for the hydrogenation and transfer hydrogenation of carbonyl compounds and other hydrogen borrowing reactions.



References:
1. J. Magano, J. R. Dunetz, *Org. Process Res. Dev.* **2012**, *16*, 1156
2. M. Yoshimura, S. Tanaka, M. Kitamura, *Tetrahedron Lett.* **2014**, *55*, 3635
3. D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621.

Computational design of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO)-based bifunctional electrodes for proton-conducting solid oxide electrochemical cells

Ana B. Muñoz-García[a], *Michele Pavone*[a]

[a] *Dipartimento di Scienze Chimiche, Università di Napoli Federico II. Email: anabelen.munozgarcia@unina.it*

Double perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO) has attracted interest in the last few years as cathode material in intermediate temperature oxide-conducting (OC) solid oxide fuel cells (SOFCs) due to its good electrochemical activity, chemical stability in red-ox conditions, and resistance to coking and sulfur poisoning.(1) By means of state-of-the art first-principles calculations, we have unveiled SFMO structural, electronic, defect and catalytic properties and propose SFMO derivatives with promising performance also in proton-conducting (PC) SOFCs. SFMO excellent performance in the OC regime can be ascribed to the easy formation of oxygen vacancies and extraordinary low oxide migration barrier heights.(2) SFMO inherent non-stoichiometry (3) turns it into a good candidate for proton conduction provided that oxygen vacancies allow the incorporation of protons into the lattice via water dissociation. Our calculations show that aliovalent doping enables convenient hydration and effective proton transport in bulk SFMO, which opens the route toward new promising triple-conducting (proton/oxide/electron) oxides for use as single-phase electrodes in PC-SOFCs.(4) Moreover, we have analyzed different reaction pathways for the performance-limiting oxygen evolution and reduction reactions (OER/ORR) and evaluated the corresponding overpotentials within the theoretical standard hydrogen electrode (TSHE) framework. (5) Beyond discussion of specific SFMO applications, we use these results on SFMO and related systems within a general framework to discuss key structural and electronic properties/processes and easily-computable descriptors that can help to design new perovskite-based electrodes for OC- and PC-SOFCs.

References

1. Q. Liu, X. Dong, G. Xiao, F. Zhao, F. Chen. Adv. Mater. 21 (2010) 5478–5482. 2. A. B. Muñoz-García, M. Pavone, A. M. Ritzmann, E. A. Carter. Phys. Chem. Chem. Phys. 15 (2013) 6250-6259. 3. A. B. Muñoz-García, D. E. Bugaris, M. Pavone, J. P. Hodges, A. Huq, F. Chen, H-C zur Loye, E. A. Carter. J. Amer. Chem. Soc. 134 (2012) 6826-6833. 4. A. B. Muñoz-García, M. Pavone. Chem. Mater. 28 (2016) 490-500. 5. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson. J. Phys. Chem. B. 108 (2004) 17886-17892.

Insight From DFT Simulations On The Collagen/Hydroxyapatite Interface: A Simple Model Based On The Poly-Proline Polymer

Cutini Michele[1*], *Marta Corno*[1] *and Piero Ugliengo*[1]

[1]*Department of Chemistry and NIS (Nanostructured Interfaces and Surfaces) Center, University of Turin, Via P. Giuria 7, 10125-Turin, (Italy)*

Collagen protein (COL) is one of the most abundant protein in mammals. Its structural peculiarity is the geometrical motif in which three parallel polypeptides strands, in a poly-proline type II (PPII) fashion, coil about each other to form a triple helix (1). COL is also the main component of bone where is in strict interaction with the hydroxyapatite mineral (HAP). Large amount of Proline (PRO) and derivatives are found in COLs. It is known that the side chain conformations of PROs have a huge role in COL features. Conformational changes between PRO puckers can lead to the COL triple helix unfolding (2). Moreover, PRO side chain mobility induces structural flexibility to the COL protein (3). In our work, we focused on the very delicate conformations of the PRO ring embedded in the COL protein. We carried out the investigations by means of accurate *ab initio* calculations by employing a very simple COL model, e.g the PPII polymer (4-5). We characterized the free PPII polymer and we simulated its adsorption on the HAP surface. We computed the relative stabilities of the PPII as free and on the HAP surface. The comparison reveals that HAP adhesion guides the formation of puckering conformers which are un-accessible by the free polymer alone.

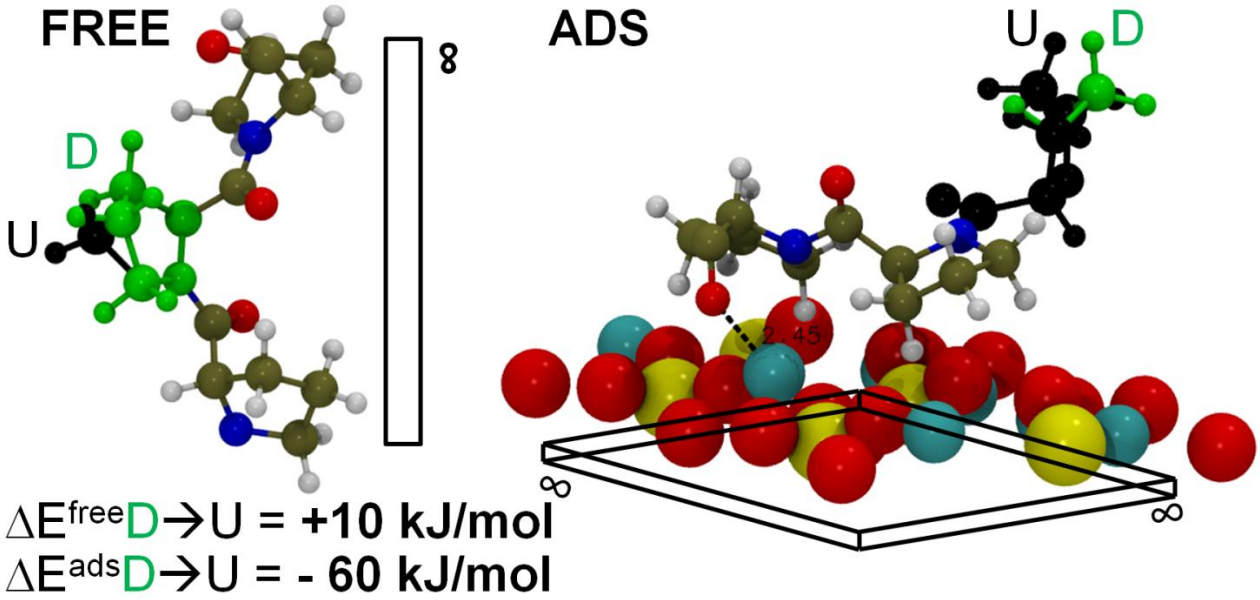


***Figure* 2.** *Difference in the relative stability for the U and D PPII conformers as free (FREE) and as adsorbed (ADS) on the HAP surface (by C=O···Ca electrostatic interaction).*

References: 1. P. Fratzl, *Collagen. Structure and Mechanics*, 2008, Springer, Postdam, Germany. 2. M. D. Shoulders, R. T. Raines, Annual Review of Biochemistry, 2009 (78) 929. 3. W. Y. Chow, D. Bihan, C. J. Forman, D. A. Slatter, D. G. Reid, D. J. Wales, R. W. Farndale, M. J. Duer, Scientific Reports, 2015 (5) 12556. 4. M. Cutini, B. Civalleri, M. Corno, R. Orlando, J. G. Brandenburg, L. Maschio, P. Ugliengo, Journal of Chemical Theory and Computation, 2016 (12) 3340. 5. M. Cutini, M. Corno and P. Ugliengo, Journal of Chemical Theory and Computation, 2017 (13) 370.

A DFT Rationalization of a Two Metals Strategy to Tune Selectivity in Catalysis

Laura Falivene[a], *Sergey Kozlov*[a] *and Luigi Cavallo*[a,b]

[a] *KAUST Catalysts Center, King Abdullah University of Science and Technology (Saudi Arabia);*
[b] *Department of Chemistry, University of Salerno (Italy); laura.falivene@kaust.edu.sa*

Selectivity is among the most important properties of an effective catalyst. In homogeneous transition metals catalysis this can be achieved by appropriate design of the ligand wrapped around the metal. In heterogeneous catalysis this is a more complex issue, since selectivity is often associated with different reactivity at different surfaces of the catalyst, as well as at steps, edges, and any type of defects that almost inevitably are present in any heterogeneous catalyst. Indeed, the less selective sites on a metallic catalyst are usually associated with low coordinated metals, such as those of rugged surfaces or defects, since these sites are considered as the most reactive. Under these conditions, a promising strategy to improve the selectivity of a metallic catalyst is alloying a second metal, less reactive and capable to occupy preferentially sites corresponding to low coordinated metals.(1) In this communication we will present some DFT insights in the dry reforming of methane promoted by Ni/Co catalysts.(2) In details, we performed DFT simulations aimed to elucidate the availability of the different active sites on the surface of the reduced CoNi particles to supplement the experimental techniques used that lack of atomic resolution.
Moreover, calculations allowed to rationalize the catalytic behavior of the alloy showing that the CoNi metal surface has an intermediate energy of oxygen chemisorption, between those of monometallic Co and Ni (see Chart 1).

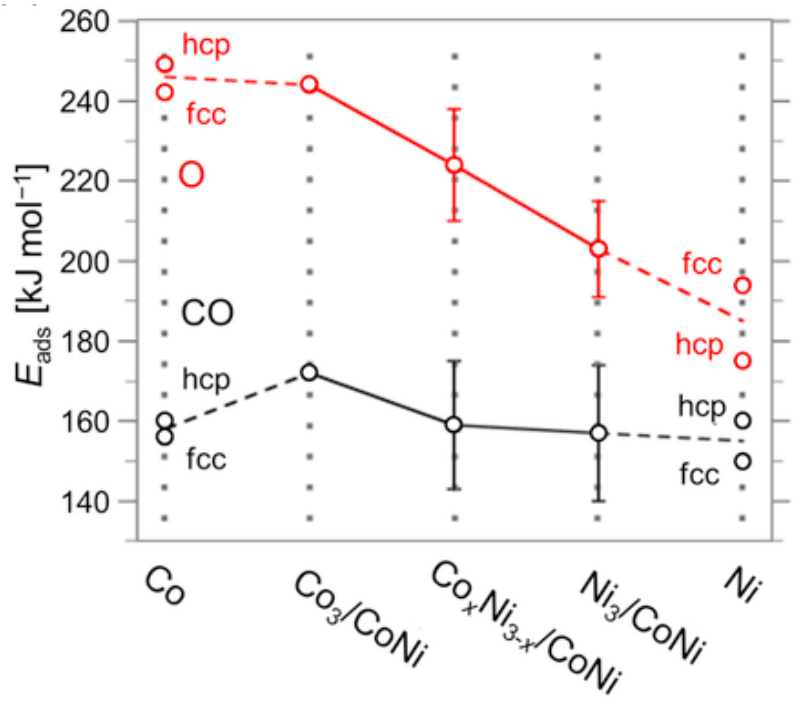


Chart 1.

References: 1. Laesgaard, E.; Clausen, B. S.;. Nørskov, J. K.; Besenbacher, F. Nature Mat. 2005, 4, 160. 2. AlSabban, B.; Falivene, L.; Kozlov, S.; Aguilar-Tapia, A.; Ould-Chikh, S.; Lahera, E.; Delnet, W.; Hazemann, J. L.; Prat, A.; Cavallo, L.; Takanabe, K.; Basset J. M. ACS Catalysis, accepted.

The role of metal substitution in the metallo-enzymes: A theoretical point of view

Tiziana Marino, Mario Prejanò, Paolo Piazzetta, Nino Russo

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, I-87036 Rende, Italy,
tmarino@unical.it

Quantum mechanical (QM) cluster model and quantum mechanical/molecular mechanical (QM/MM) calculations were performed on some metalloenzymes belonging to different classes. Insight is gained into the enzymatic activity upon metal-ion substitution.

The examined cases:

-Carbonic anhydrase (CA): Zn-, Co-, Cd-CA hydrating CO_2;(1,2) Rh-CA hydrogenating CO_2 to formic acid. (3)

-Methanol dehydrogenase (MDH): Ce(III)-MDH versus Ca(II)-MDH. (4)

References: 1. P. Piazzetta, T. Marino, N. Russo, and D. R. Salahub *ACS Catal.* **5**, 2015, 5397−5409. 2. P. Piazzetta, T. Marino, N. Russo, and D. R. Salahub *ChemCatChem* 2017, 9, 1047–1053. 3. P. Piazzetta, T. Marino, N. Russo, and D. R. Salahub *Coordination Chemistry Review*, 2017, ISSN: 0010-8545 DOI:10.1016/j.ccr.2016.12.014. 4. M. Prejanò, T. Marino and N. Russo *Chemistry*, 2017, dx.doi.org/10.1002/chem.201700381.

Back-donation in d^0 Metal Complexes: Does it Exist? The case of Nb(V)

Gianluca Ciancaleoni[a], *Niccolò Bartalucci*[a], *Leonardo Belpassi*[b], *Fabio Marchetti*[a]

[a] *Università degli Studi di Pisa, Dipartimento di Chimica e Chimica Industriale, via Giuseppe Moruzzi, 13 - 56124 Pisa, Italy*

[b] *Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), c/o Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto 8, I-06123 Perugia, Italy*

Since the introduction of the Dewar-Chatt-Duncanson (DCD) model, which almost 70 years ago proposed an elegant framework to rationalize the coordination of an olefin to a transition metal, inorganic chemists expanded its use to the coordination of every ligands, including carbon monoxide, phosphines and carbenes, demonstrating its general applicability.

Particularly interesting is the bonding in d^0 metal complexes: in the simplest sense, they should not be able to back-donate electronic density to the ligand because their *d* orbitals are formally empty, but, obviously, things are more complex than this. For example, $[Cp^*_2M(H)_2CO]$ complexes (M = Zr, Hf) exhibit a classical behavior (υ_{CO} = 2044 and 2036 cm^{-1} for Zr(IV) and Hf(IV), respectively) (1) and it has been proposed that "back-donation" could come from a M-H orbital of appropriate symmetry.

Recently, various Nb(V)-carbene complexes have been structurally characterized(2) and all of them exhibit a peculiar metal arrangement: the halides *cis* to the carbene that lie almost perpendicular to the plane of the carbene are slightly bent toward the carbene itself. According to some authors, this is an evidence of Cl → carbene back-donation, but according to others, the Nb-carbene bond is a pure σ bond.

In this contribution, we shed some light on this controversial topic through a combined experimental/theoretical approach, studying complexes with appropriate ligands and analyzing their Nb-L bond by means of the Charge Displacement analysis, which recently demonstrated its potential in the detailed and quantitative characterization of coordinative bonds.(3)

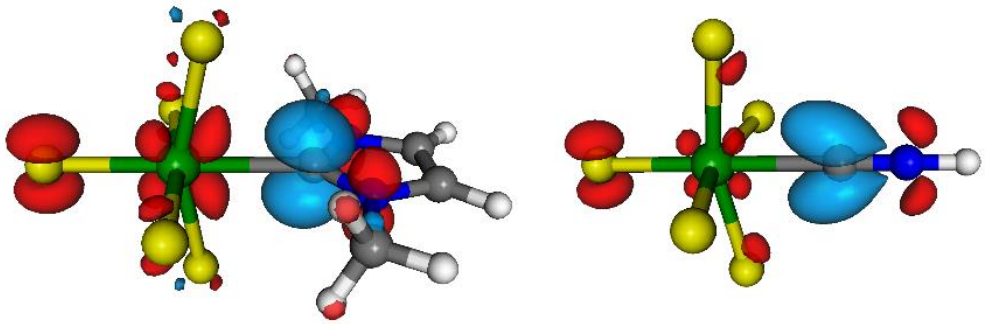


Figure: Isodensity surfaces (±0.001 e/a.u.) for the B1 component of the density deformation function upon the formation of the $[NbCl_5]$-L bond (L = 1,3-dimethyl-imidazol-2-ylidene, hydrogen isocyanate).

References:

1. (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw., J. E. *J. Am. Chem. Soc*. 1976, 6733; (b) Marsella, J. A.; Curtis, J. C.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc*. 1980, 7244.
2. (a) Bortoluzzi, M.; Ferretti, E.; Marchetti, F.; Pampaloni, G.; Zacchini, S. *Chem. Commun*. 2014, 4472; (b) Bortoluzzi, M.; Ferretti, E.; Marchetti, F.; Pampaloni, G.; Zacchini, S. *Dalton Trans*. 2016, 6939.
3. (a) Bistoni, G.; Rampino, S.; Scafuri, N.; Ciancaleoni, G.; Zuccaccia, D.; Belpassi, L.; Tarantelli, F., *Chem. Sci.* 2016, 1174; (b) Ciancaleoni, G.; Biasiolo, L.; Bistoni, G.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D.; Belpassi, L. *Chem. Eur. J.* 2015, 2467.

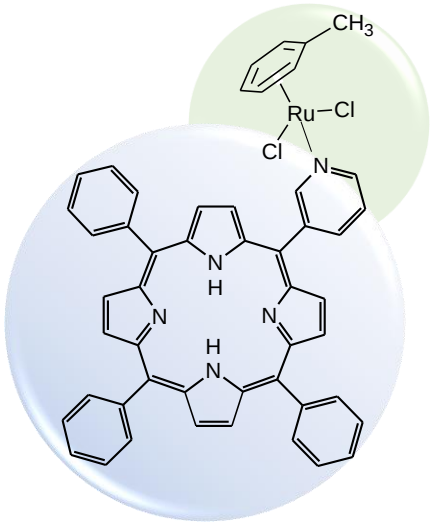
Combination of Porphyrin and Ruthenium-arene moieties for a Dual Anticancer Function. A Theoretical Investigation.

Gloria Mazzone[a], *Claudia Regina*[a], *Nino Russo*[a]

[a] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036 Arcavacata di Rende (CS); gloria.mazzone@unical.it*

Combining therapies for the treatment of diseases has become a worthwhile strategy to improve efficiency and decrease side effects. In particular against cancer, a combination of chemotherapeutics with radiation is recently appeared as a common form of treatment. It requires the photosensitizing action of a molecule able to absorb a radiation with appropriate wavelength and a metal complex demanded to exert the chemotherapeutic function.

As regards the metal complex, several efforts have been devoted in the last years to find an alternative to cisplatin anticancer, whose clinical effectiveness has been greatly limited by drug resistance and significant side effects. In the search for new metal based anticancer agents ruthenium complexes have raised great interest, and their antitumor potential has been established over two decades ago. Thus, a huge variety of plausible complexes able to inhibit tumor cells growth have been proposed, some of them are under clinical trials.[1]



From the other hand, photosensitizers currently approved for clinical use in photodynamic therapy belong to the porphyrin-like class of molecules thanks to their low dark toxicity, thermodynamic stability, absorption properties in the Q band that can be modulated by varying π electrons and facility to form metal complexes or to include in their structures heavy atoms.

Recently some Ru-based complexes, as that depicted in figure, have been suggested as drug candidates toward human melanoma cancer cells, due to their dual synergistic effect of the arene ruthenium chemotherapeutics and the porphyrin photosensitizer.[2]

Previous studies have largely demonstrated that theoretical computations based on first-principles methods can reliably predict or reproduce and rationalize electronic transitions,[3-8] as well as can give further insight into the mechanisms involved in the drug action.[9,10]

Density Functional Theory and its time-dependent formulation (TD-DFT) have been used to shed light on the mechanism of action of these compounds, exploring their photophysical properties and the mechanistic features.

References:
1. C. Mari, V. Pierroz, S. Ferrari, G. Gasser, *Chem. Sci.* **2015**, 6, 2660.
2. F. Schmitt, P. Govindaswamy, O. Zava, G. Sűss-Fink, L. Juillerat-Jeanneret, B. Therrien, *J. Biol. Inorg. Chem.* **2009**, 14, 101.
3. G. Mazzone, N. Russo, E. Sicilia, *Can. J. Chem.* **2013**, 91, 902.
4. M. E. Alberto, B. C. De Simone, G. Mazzone, A. D. Quartarolo, N. Russo, *J. Chem. Theory Comput.* **2014**, 10, 4006.
5. M. E. Alberto, B. C. De Simone, G. Mazzone, E. Sicilia, N. Russo, *Phys.Chem.Chem.Phys.* **2015**, 17, 23595.
6. G. Mazzone, A. D. Quartarolo, N. Russo, *Dyes and Pigments* **2016**, 130, 9.
7. G. Mazzone, M. E. Alberto, B. C. De Simone, T. Marino, N. Russo, *Molecules* **2016**, 21, 288.
8. J. Pirillo, G. Mazzone, N. Russo, L. Bertini, *J. Chem. Inf. Model.* **2017**, 57, 234.
9. I. Ritacco, N. Russo, E. Sicilia, *Inorg. Chem.* **2015**, 54, 10801.
10. I. Ritacco, G. Mazzone, N. Russo, E. Sicilia, *Inorg. Chem.* **2016**, 55, 1580.

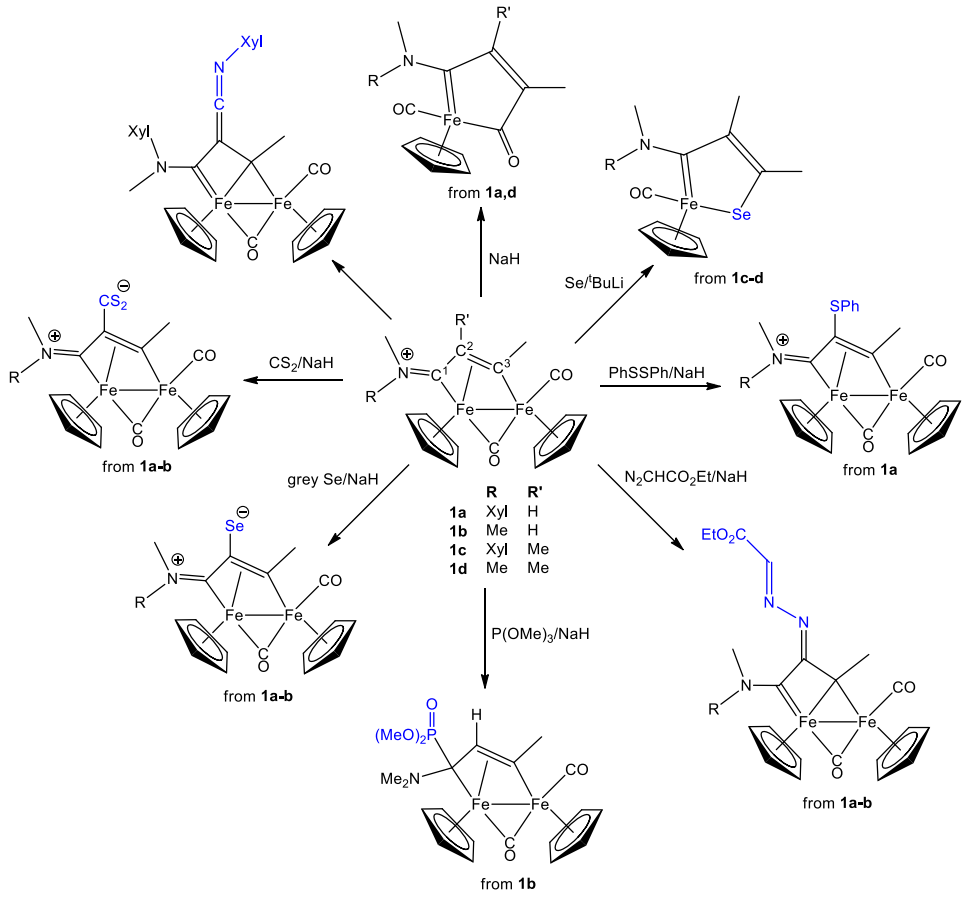
Comunicazioni Poster

In vitro Anticancer Activity of Diiron Vinyliminium Complexes

Gabriele Agonigi[a], *Lucinda K. Batchelor*[b], *Paul J. Dyson*[b], *Fabio Marchetti*[a], *Guido Pampaloni*[a], *Stefano Zacchini*[c], *Valerio Zanotti*[c]

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, I-56124 Pisa (Italy); Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne (Switzerland); Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4, I-40136 Bologna (Italy); E-mail:g.ago2@hotmail.it*

Vinyliminium ligands, bridging coordinated in diiron carbonyl complexes (1,2), can undergo a variety of functionalization reactions driven by the cooperative effects of the two adjacent metal centres (Scheme)[1]. The antiproliferative activity of a number of air and water stable derivatives has been assessed towards the cisplatin sensitive A2780 and the cisplatin resistant A2780cisR human ovarian carcinoma cell lines. The results will be discussed with reference to possible structure-activity relationship; in particular, those compounds containing a N-bound xylyl substituent exhibit considerable cytotoxicity.



References: 1. R. Mazzoni, M. Salmi and V. Zanotti, *Chem. Eur. J.* **2012**, *18*, 10174-10194. 2. V. Zanotti, Pure Appl. Chem., 2010, 82, 1555–1568.

Self-assembling peptides for regenerative medicine: structural characterization and biological properties.

Chiara Battocchio[a], Valeria Secchi[a], Stefano Franchi[a], Marta Santi[a], Ilaria Fratoddi[b], Iole Venditti[b], Monica Dettin[c], Brigida Bochicchio[d], Giovanna Iucci[a],

[a] Department of Science, ROMA TRE University, Viale Vasca Navale 79, 00146, Rome (IT); [b] Department of Chemistry, La Sapienza University P.le A. Moro 5, 00187 Rome (IT); [c]Department of Industrial Engineering, University of Padua, Via Marzolo, 9, 35131, Padua, (IT); [d] Department of Science, University of Basilicata, Via Ateneo Lucano 10, 85100, Potenza (IT)
chiara.battocchio@uniroma3.it

The main object of regenerative medicine is to develop novel therapies to replace or restore function to tissues and organs within the human body [1]. In this context, self-assembling peptides (SAPs) are an appealing class of materials, due to their ability to organize in nanostructures that can be successfully anchored to appropriate substrates or directly injected into a lesion [2]. SAPs are able to mimic the structure of the extra-cellular matrix (ECM), offering tridimensional support for cell growth [3,4]. Indeed, these nanomaterials, eventually functionalized with signaling biomolecules (growth factors, small adhesive peptidic sequences, glycans) may constitute a biomimetic matrix with the ability of surrounding cells and promoting specific interactions with them, in order to control and conduct their behavior by mimicking their native environment. The ideal matrix must have a 3D geometry similar to the extracellular matrix and must be able to promote cell adhesion, proliferation, infiltration and differentiation aimed at new tissue formation [4]. The realization of self-assembling peptides must include a first step of chemical and structural characterization, to check the stability of the molecular structure following the scaffold's development. In the present study we have chemically characterized different type of peptides using X-ray photoelectron spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure (NEXAFS) also in angular-dependent mode, Fourier Transform Infrared Spectroscopy (FT-IR) both in transmission and total reflection mode (IRRAS) with the aim to probe the chemical composition, molecular structure and conformation of the proposed materials.
The second step of this work consists in an accurate investigation of the biological properties of SAPs and their interaction with cells. For this reason cells were cultured in the presence of the SAPs in order to assess if peptides exert cytotoxic effect and to evaluate biocompatibility, cellular adhesion and proliferation.

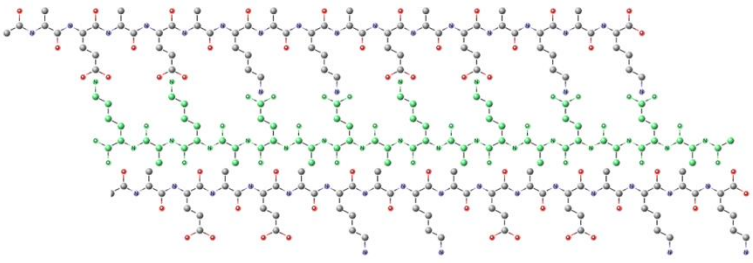


Figure 1. Chemical structure of a self-assembling peptide

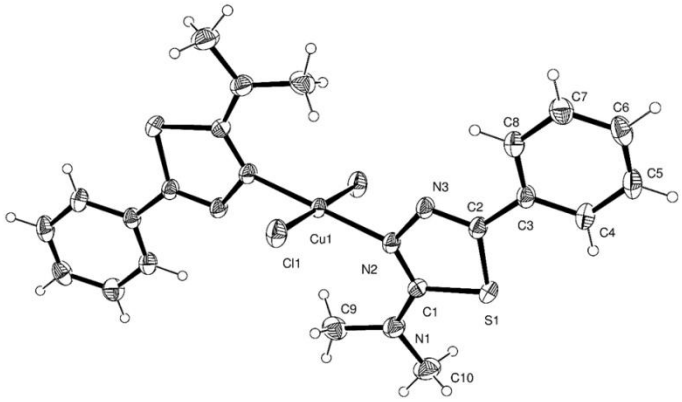
References:
1. Kobolak J., Dinnyes A., Memic A., Khademhosseini A., Mobasheri A. Methods; 2015.
2. Dettin M., Zamuner A., Iucci G., Messina G.M.L., Battocchio C., Picariello G., Gallina G., Marletta G., Castagliuolo I., Brun P. Journal of Peptides Science 2014.
3. Flamia R., Salvi A.M., D'Alessio L., Castle J.E., Tamburro A.M. Biomacromolecules 2007, 8, 128-38.
4. Secchi V., Franchi S., Fioramonti M., Polzonetti G., Iucci G., Bochicchio B., Battocchio C. Materials Science and Engineering: C, 77 (2017) 927–934.

Thiosemicarbazones and their copper complexes: evaluation of antifungal and anti-aflatoxin activity for the development of novel plant protection products

M. Carcelli[a], D. Rogolino[a], G. Pelosi[a], F. Bisceglie[a], J. Bartoli[a], F. M. Restivo[a], F. Degola[a], A. Buschini[a], S. Montalbano[a], D. Feretti[b], C. Zani[b]

[a]Dip. Scienze Chimiche, della Vita e della Sostenibilità Ambientale. Consorzio Interuniv. Ricerca Chimica dei Metalli nei Sistemi Biologici, Università di Parma, Parco Area delle Scienze, 43124 Parma. [b] Dip. Specialità medico-chirurgiche, scienze radiologiche e sanità pubblica, Università di Brescia, Viale Europa 11, 25123 Brescia; E-mail: mauro.carcelli@unipr.it

Food security and preservation is an ongoing major concern. It is estimated that about 40% of the food produced worldwide is lost or spoiled. One of the most important cause of food spoilage is related to the presence of fungi, in particular of *Aspergillus*, *Penicillium*, *Fusarium* and *Alternaria* genera (1). These fungi are the principal producers of aflatoxins (AF), secondary metabolites with a severe toxic and carcinogenic potential. Concerns on food safety and environmental health, combined with the issue of emerging resistant pest strains, make urgent to develop novel crop-protective agents. Some studies suggested that metal ions can influence the growth and the mycotoxin production of the toxigenic fungi and that this effect can be related to the ability of metal ions to intervene on the pattern of gene expressions of *A. flavus* (2). Metal chelation could improve lipophilicity, facilitating the penetration of the complexes into lipid membranes, and should restrict proliferation of the microorganisms. Thiosemicarbazones represent a very attractive class of metal-chelating ligand for their coordinating versatility and their known antifungal activity (3). Here the evaluation of the antifungal and anti-aflatoxin activity towards *A. flavus* of some thiosemicarbazones ligands, derived from the vanillin scaffold, and of their metal complexes are presented. The metal complexes were studied both in solution and at the solid state (the complex in figure is the product of the cyclic oxidation of the ligand during the reaction with $CuCl_2$). Tests to assess cyto- and geno-toxic effects on human cells were performed on the most active compounds. Best hits were also evaluated for their toxic and mutagenic activities on bacteria and plants cells.



This work is supported by Fondazione Cariplo - Project N. 2014-0555, http: www.aflatox.it.

References:

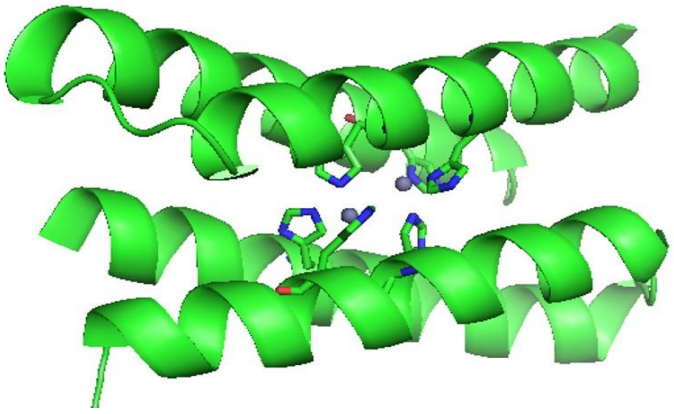
1. Tournas V H, Critical reviews in microbiology (2005) 31, 33-44.
2. Cuero, R et al. J. Appl. Microbiol. (2003) 94, 953–961. doi:10.1046/j.1365 2672.2003.01870.x
3. Degola F et al. J. Food Microbiol. (2015) 200, 104-111. doi: 10.1016/j.ijfoodmicro.2015.02.009

De novo design of a dinuclear copper protein with diphenolase activity

Chino M[a], Pirro F[a], Leone L[a], Nastri F[a], Maglio O[b], Pavone V[c], Lombardi A[a]

[a] Department of Chemical Sciences, University of Naples "Federico II", Via Cintia, 80126 Naples, Italy; [b] IBB, CNR, Via Mezzocannone 16, 80134 Naples, Italy; [c] Department of Biology, University of Naples "Federico II", Via Cintia, 80126 Naples, Italy. Email: marco.chino@unina.it

The type III copper center (T3) consists of a binuclear copper site; its main role in biology is the binding of molecular oxygen and, eventually, its subsequent activation (1).
The metal site is characterized by two magnetically coupled copper ions that bind dioxygen in a symmetric, side on (μ-η^2:η^2) fashion, which exhibits unique spectral features. Each copper ion is bound in a nearly planar trigonal geometry by three histidine residues, provided by an antiparallel α-helix pair.
Several synthetic compounds, bearing the side-on peroxo-Cu(II)$_2$ (Cu_2O_2) core, confirmed its capability to perform an electrophilic σ* attack to a properly oriented aromatic ring (2). Stack and coworkers have managed to recreate the core through the self-assembly of monodentate imidazole ligands and to prove its innate ability to hydroxylatate phenolic substrates (3). However, the Cu_2O_2 core has not yet been reported in water under mild conditions.
To shed light on the obstacles that Nature faced in stabilizing and tuning the metal core under physiological conditions, a model peptide was designed using a *de novo* approach. The previously designed DFs (*Due Ferro*), a series of artificial proteins inspired to natural di-iron proteins, have been exploited as starting scaffold. DFs self-assemble into an antiparallel four-helix bundle dimer and bind two iron ions in the protein core (4).
The coordinating and the second sphere residues were modeled in an attempt to reconstruct a type III copper center. The final model was evaluated through MD simulations, leading to the DR1 (*Due Rame*) sequence.
DR1 is a dimer in the *apo*-form, and binds two copper ions as expected. More importantly, DR1 catalyzes the oxidation of 3,5-di-tert-butyl catechol to the corresponding o-quinone, cycling between Cu(I) and Cu(II) under mild conditions. Nevertheless, further effort should be paid for a finer positioning of the two copper ions to obtain the Cu_2O_2 core.
In perspective, the diphenolase activity of DR1 paves the way for numerous biotechnological applications in environmental technology and in pharmaceutical industries (5).



References: 1. Decker, H. et al. *J. Exp. Biol.* **2002**, 203, 1777–1782; 2. Itoh, S. et al. *Acc. Chem. Res.* **2007**, 40 (2), 592–600; 3. Citek, C. et al. *Nat. Chem.* **2012**, 4, 317–322; 4. Chino, M. et al. *Eur. J. Inorg. Chem.* **2015**, 21, 3371–3390; 5. Nastri, F. et al. *Chem. Soc. Rev.* **2016**, 0, 1-35

Structural characterization and reactivity of bare cis- and transplatin hydrolysis products

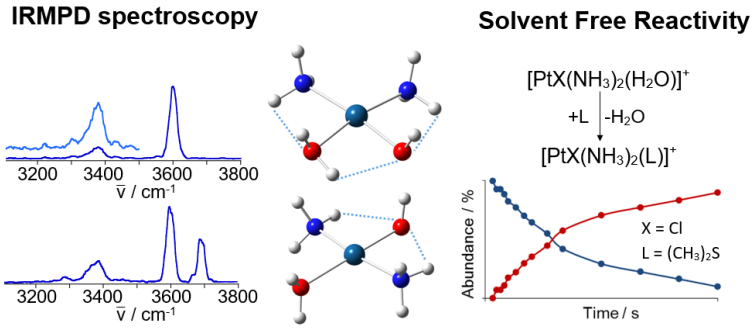
Davide Corinti[a], *Cecilia Coletti*[b], *Nazzareno Re*[b], *Susanna Piccirillo*[c], *Marco Giampà*[ad],*Maria Elisa Crestoni*[a], *Simonetta Fornarini*[a]

[a] *Università degli Studi di Roma "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy;* [b] *Università G. D'Annunzio, Via dei Vestini 31, I-66100 Chieti, Italy;* [c] *Università di Roma "Tor Vergata", via della Ricerca Scientifica, 00133 Rome, Italy;* [d] *Centrum fur Biotechnologie (CeBiTec), Universitat Bielefeld, Universitatsstraße 27, Bielefeld, Germany. Email: davide.corinti@uniroma1.it*

Cisplatin (*cis*-$[PtCl_2(NH_3)_2]$) is a widely used antineoplastic drug, particularly effective in the treatment of lung and prostate solid tumors. Its activity relies on the interaction with the nucleobases of DNA, in particular adenine and guanine, leading to inhibition of transcription and eventually cell death.(1-3) However, the actual active species are recognized to be the products of cisplatin aquation (substitution of Cl^- with H_2O), making a matter of great interest the understanding of the reactivity of these aquated complexes.(4) In this context, the use of a solvent-free environment permits to obtain an unambiguous characterization of these ions, while prototropic equilibria and the formation of hydroxo-bridged polinuclear complexes make hard to achieve the same result in water solution.

In this contribution we present a thorough characterization of the geometrical features of cisplatin and its geometrical isomer transplatin hydrolysis products, obtained using IR multiple photon dissociation spectroscopy in the X-H (X = C, N, O) stretch region (3000-3700 cm^{-1}) and quantum mechanics calculations.(5,6)

Moreover, cis- and transplatin aquated and diaquated species were mass-selected and allowed to interact with several neutral molecules in the cell of an FT-ICR mass spectrometer to obtain kinetic information about gas-phase reactivity. Chosen molecules were representatives of cisplatin binding motifs with biological targets, e.g. pyridine for nucleotides, thioanisole and dimethylsulfide for thiol-containing amino-acid residues and trimethylphosphate for ubiquitous inorganic phosphates as well as for phosphate groups present in the backbone of nucleic acids. The kinetic data showed a consistently higher reactivity for the primary aquation product of both cis- and transplatin ($[PtCl(NH_3)_2(H_2O)]^+$) compared with the complexes that have experienced a second hydrolysis process ($[Pt(OH)(NH_3)_2(H_2O)]^+$). Differences in reactivity between the *cis* and *trans* isomers are also critically discussed comparing geometrical features and employing potential energy surface calculations.



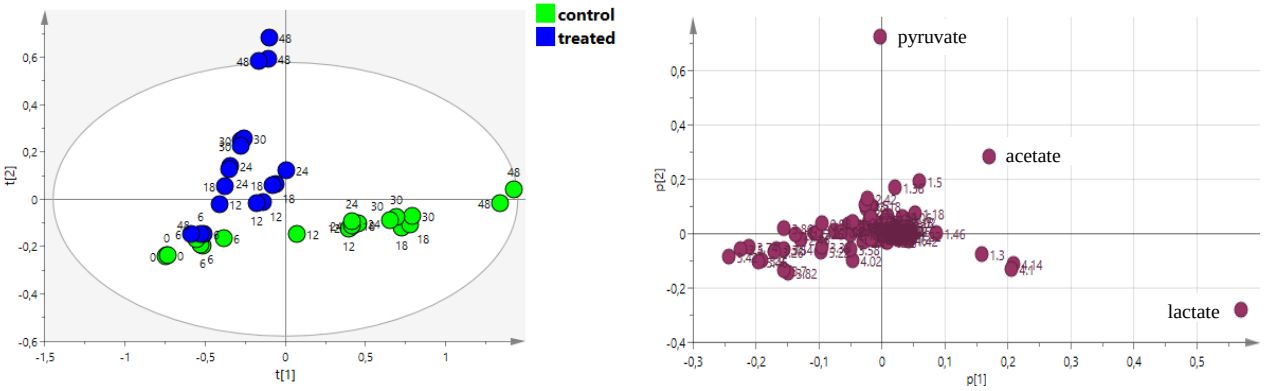
References: 1. A.V.Klein, T.W.Hambley *Chem. Rev.* **2009**, *109*, 4911. 2. B.Chiavarino, M.E.Crestoni, S.Fornarini, D.Scuderi, J.Y.Salpin *J. Am. Chem. Soc.* **2013**, *135*, 1445. 3. B.Chiavarino, M.E.Crestoni, S.Fornarini, D.Scuderi, J.Y.Salpin *Inorg. Chem.* **2015**, *54*, 3513. 4. M. S. Davies, S. J. Berners-Price, T. W. Hambley *Inorg. Chem.* **2000**, 39, 5603–5613. 5. A. De Petris, A. Ciavardini, C. Coletti, N. Re, B. Chiavarino, M. E. Crestoni, S. Fornarini *J. Phys. Chem. Lett.* **2013**, 4, 3631–3635. 6. D. Corinti, C. Coletti, N. Re, S. Piccirillo, M. Giampà, M. E. Crestoni, S. Fornarini *RSC Adv.* **2017**, 7, 15877.

[Pt(*O,O'*-acac)(γ-acac)(DMS)] antitumour activity on epithelial ovarian carcinoma cells resistant to *cisplatin*: ^{1}H NMR metabolomic study

Federica De Castro[a], *Michele Benedetti*[a], *Giovanna Antonaci*[a], *Laura Del Coco*[a], *Sandra Angelica De Pascali*[a], *Santo Marsigliante*[a] *and Francesco Paolo Fanizzi*[a]

[a] *Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Monteroni, I-73100 Lecce, Italy. e-mail: federica.decastro@unisalento.it*

Epithelial ovarian carcinoma (EOC) is the principal cause of death among women (1). Actually, the treatment of advanced ovarian cancer consists of combinations of a maximal surgical effort together with chemotherapic approaches based on the sinergic action of taxanes and various platinating agents. Unfortunately, notwithstanding such new therapeutic approaches the overall 5-year survival still remains unsatisfying, being of about 44% (2). The main problems in the treatment of EOC are the necessity of an early diagnose, together with the ability to circumvent the acquired on intrinsic resistance of some EOC tumours. For this reason, it is very important the research of valid alternatives to currently used chemotherapic approaches. The [Pt(*O,O'*-acac)(γ-acac)(DMS)], **1**, is a recently synthesized compound (3) containing two acetylacetonates and one dimetylsulphide (DMS) ligands in the metal coordination sphere. This complex demonstrated interesting biological activities, produced by the capability to cross efficiently the plasma cell membranes. Consistently, it was measured a cytotoxicity level more than 10 times higher than that of *cisplatin*. This was recognized in several cell types (4-6) where, differently from *cisplatin*, the involvement of non genomic targets was also identified. It clearly indicates the existence of mechanisms of action different from that of *cisplatin* (6). In this work, we evaluated the activity of complex **1** on the Skov-3 cells being an EOC cell line resistant to *cisplatin*. At this regard, we first made MTT assays, to evaluate the antitumour efficacy of complex **1** on the Skov-3 cells. Then, we examined cellular extracts and culture media, by using a ^{1}H NMR based metabolomic approaches, see Figure. In this way, we could identify the metabolic variations, induced by complex **1** on the Skov-3 cells, which show the possible pathways involved in the antitumour activity.



References: 1. A. Jemal, R. Siegel, E. Ward et al., "Cancer statistics, 2006," *CA: A Canc. J. for Clinicians*, 2006, 56 (2), 106–130. 2. R. F. Ozols, B. N. Bundy, B. E. Greer, J. M. Fowler, D. Clarke-Pearson, R. A. Burger, et al. *J Clin Oncol*, 2003, 21(17), 194–200. 3. S. A. De Pascali, P. Papadia, A. Ciccarese, C. Pacifico, F. P. Fanizzi. *Eur J Inorg Chem*, 2005, 788–96. 4. A. Muscella, N. Calabriso, S. A. De Pascali, L. Urso, A. Ciccarese, F. P. Fanizzi, D. Migoni and Marsigliante S. *Biochem Pharmacol* 2007, *74*, 28-40. 5.Muscella A, Calabriso N, De Pascali SA, Urso L, Ciccarese A, F. P. Fanizzi, D. Migoni and S. Marsigliante *Brit. J. Pharmacol*, 2008, 153, 34-39. 6.A. Muscella, C. Vetrugno, F. Biagioni, N. Calabriso, M. T. Calierno, F. Fornai, S. A. De Pascali, S. Marsigliante, F. P. Fanizzi, British *J. of Pharmacology* 2016, 173(17), 2633-2644. 7.C. Fenoglio, F. Albicini, S. A. De Pascali, G. Milanesi, M. Fumagalli, D. Migoni, F. P. Fanizzi and G. Bernocchi *Metal-Based Drugs*, 2011, 1-10.

Passive and Active Bone-Targeting of the Pt-based Antitumor Drug Kiteplatin.

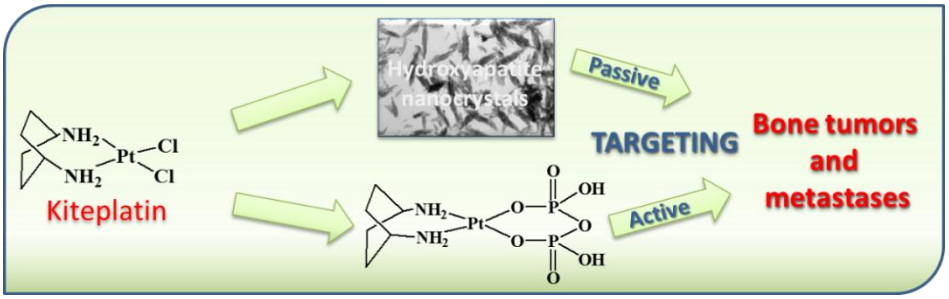
Giovanni Natile,[a] *Nicola Margiotta*,[a] *Alessandra Curci*,[a] *Graziano Fusillo*,[a] *Valentina Gandin*,[b] *Cristina Marzano*,[b] *Marcol Lelli*,[c] *Norberto Roveri*.[c]

[a]*Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Bari (Italy);* [b]*Dipartimento di Scienze del Farmaco, Università di Padova, Padova (Italy) ;* [c] *Bioecoactive S.r.l, via San Donato n.5, 40050 Granarolo (Italy). Email: giovanni.natile@uniba.it*

Platinum-based antitumor drugs, such as cisplatin carboplatin, and oxaliplatin, have poor pharmacokinetic profile and their un-specific distribution in the body leads to systemic toxicity. Therefore, it is highly desirable to develop antitumor Pt-complexes with ligands specific to target the tumor site. In addition, nanoparticle formulations allow the preferential delivery of drugs to the tumor site since they can take advantage of the leaky vasculature surrounding the malignant tissue (Enhanced Permeability and Retention effect).

We have been involved in the preparation of bone-targeted platinum-bisphosphonate anticancer drugs and their subsequent loading onto inorganic silica xerogels or hydroxyapatite (HA) nanocrystals with the aim of using these matrices for the local treatment of bone tumors.(1) In the present study, we have investigated the adsorption on and the release from biomimetic HA nanocrystals of kiteplatin [$PtCl_2$(*cis*-1,4-DACH)] (DACH = diaminocyclohexane) and of its 1,1-cyclobutanedicarboxylate derivative [Pt(CBDCA)(*cis*-1,4-DACH)]. The release has been investigated as a function of pH to mimic the different physiological environments of healthy (including blood) and tumor tissues and the *in vitro* cytotoxicity of the releasates from the HA matrices has been assessed against various human cancer cell lines.(2)

Moreover, active targeting of kiteplatin towards bone tumors has been pursued by preparing two new pyrophosphate derivatives that resulted to be activated at acidic pH and hence at the hypoxic and low-pH environment surrounding a tumor mass. The two kiteplatin-pyrophosphate derivatives have also been tested *in vitro* to assess their cytotoxicity against a panel of human tumor cell lines.(3)



Acknowledgments

We acknowledge the University of Bari (Italy), the Italian Ministero dell'Università e della Ricerca, the Inter-University Consortium for Research on the Chemistry of Metal Ions in Biological Systems (C.I.R.C.M.S.B.) for support.

References

1) a) Iafisco, M.; Margiotta, N. J. Inorg. Biochem. 2012, 117, 237–247. b) K. Farbod, K. Sariibrahimoglu, A. Curci, A. Hayrapetyan, J.N.W. Hakvoort, J.J.J.P. van den Beucken; M. Iafisco, N. Margiotta, S.C.G. Leeuwenburgh. Tissue Eng. - Part A 2016, 22, 788-800.

2) Lelli, M.; Roveri, N.; Marzano, C.; Hoeschele, J. D.; Curci, A.; Margiotta, N.; Gandin, V.; Natile, G. Dalton Trans. 2016, 45, 13187–13195.

3) Curci, A.; Gandin, V.; Marzano, C.; Hoeschele, J.D.; Natile, G.; Margiotta, N. 2017, submitted.

Valproic acid and cisplatin: comparison among different ways to combine them

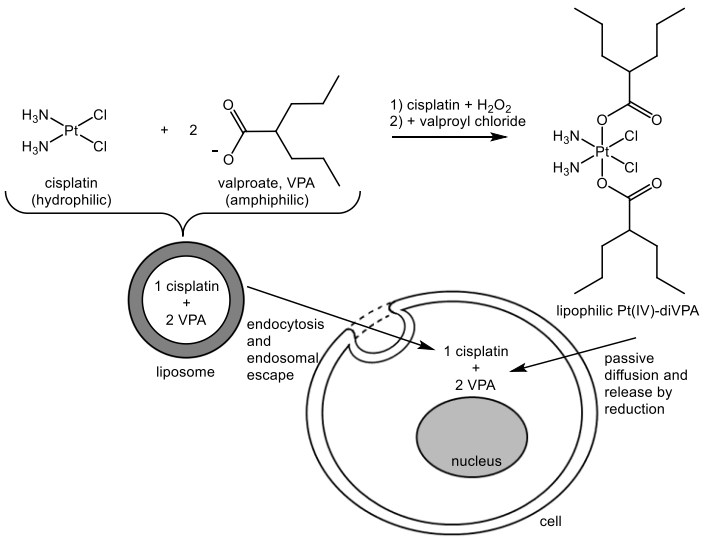
Elena Perin[a], Elisabetta Gabano[a], Ilaria Zanellato[a], Andrea Gallina[a], Mauro Ravera[a], Domenico Osella[a]

[a]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, viale T. Michel, 11, 15121 Alessandria, Italy; E-mail: elena.perin@uniupo.it

Malignant pleural mesothelioma (MPM) is an aggressive tumor of the mesothelial cells that line the pleural cavity and is associated to the exposure to asbestos fibers. The Food and Drug Administration accepted the combination of cisplatin and pemetrexed as a treatment which only partially extends the mean survival. Since epigenetic modifications play a significant role in neoplastic progression, the research aims to co-administer a drug with this function, with another chemotherapeutic. One of the epigenetic modifications is the acetylation of histones (structural components of chromatin), controlled by histone acetyltransferases and histone deacetylases (HDAC). HDAC remove the acetyl groups from the histone, increasing its association with DNA. For this reason, HDAC inhibitors can favor the binding of a drug to its DNA target. Moreover, the acetylated histones can activate the transcription of some genes with following inhibition of tumor growth and apoptosis (1).

Even though cisplatin and its analogues are important antitumor drugs, many side effects and deactivation processes occur. To overcome these limits, the higher inertness of the Pt(IV) complexes can be exploited. They are reduced to their corresponding Pt(II) active metabolite in the hypoxic and reducing tumor *milieu*: for this reason, they are considered prodrugs. Furthermore, passive Drug Targeting and Delivery (DTD) strategies can be developed to improve the selective accumulation of such species. The increased vascular permeability of the tumor tissue and the reduced drainage of the lymphatic system allow macromolecules (e.g. nanoparticles, liposomes, etc.) to extravasate and to be retained for long time. Therefore, nanosized carriers can be used as carriers of drugs towards the tumor tissue.

This work aims to combine cisplatin and valproic acid, a HDAC inhibitor (2). In particular, cationic liposomes containing cisplatin, valproate or the 1:2 combination of both drugs were synthesized and tested on tumor cells to evaluate if the co-administration of the two species encapsulated either into the same liposome or into separated lipid vectors allows to obtain the same antiproliferative effect of a Pt(IV) complex, containing valproates as axial ligands (Pt(IV)-diVPA in Figure). This latter proved to have a high cytotoxic activity on several tumor cell lines, higher than cisplatin(3).



References:

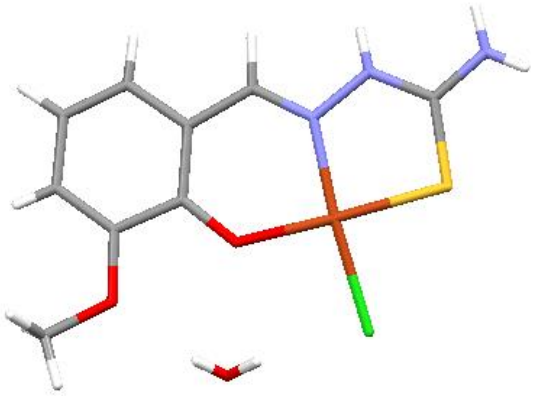
1. S. A. Bassett, M. P. G. Barnett, *Nutrients*, 6, **2014**, 4273-4301.
2. M. Ravera, E. Gabano, I. Zanellato, A. Gallina, E. Perin, A. Arrais, S. Cantamessa, D. Osella, *Dalton Trans.*, 46, **2017**, 1559-1566.
3. M. Alessio, I. Zanellato, I. Bonarrigo, E. Gabano, M. Ravera, D. Osella, *J. Inorg. Biochem.*, 129, **2013**, 52-57.

Anti-proliferative effects of copper(II) complexes with tridentate thiosemicarbazone ligands

D. Rogolino[a], M. Carcelli[a], G. Pelosi[a], M. Tegoni[a], V. Gandin[b]

[a] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale and Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici, Università di Parma, Parco Area delle Scienze, 43124 Parma, Italy. [b]Dipartimento di Scienze del Farmaco, Università di Padova, Via Marzolo 5, Padova, Italy; E-mail dominga.rogolino@unipr.it

The therapeutic use of cisplatin, the drug actually employed against various types of cancer, is hampered by the presence of adverse effects and the occurrence of resistance (1,2). These reasons have stimulated extensive research towards other metal-based anti-tumor compounds with improved pharmacological properties. In this context, the use of essential metals such as copper can lead to the development of less toxic and more effective drugs (3). Thiosemicarbazones (TSCs) are a class of compounds that have been studied for a long time due to their biological properties (4). TSCs can lead to interesting compounds with potent cytotoxicity towards cancer cells and low toxicity for healthy cells, as demonstrated by the studies on Triapine™ (3-aminopyridine-2-carboxyaldehyde-TSC), that entered phase II of clinical trials against many types of cancer (5).
Here we report the synthesis and characterization, both in solution and at the solid state, of novel copper(II) complexes of O,N,S-tridentate TSC ligands (the X-ray structure of one of them is reported in figure below). The antiproliferative activity of the complexes has been studied in two-dimensional and three-dimensional cell cultures. Cytotoxicity tests were conducted against a large panel of human tumor cell lines of different histology. The obtained data allowed to formulate some preliminary structure-activity relationships. In order to correlate the cytotoxic effect promoted by the compounds under investigation with their intracellular accumulation, cell uptake experiments were also conducted. Furthermore, we investigated the mechanism of action at the base of their anti-tumor activity *in vitro* by appropriate biochemical and microscopy tests.



References:
1. Kelland L. Nat. Rev. Cancer, 2007, 7, 573-84
2. Zhang C.X., Lippard S.J. Curr. Opin. Chem. Biol., 2003, 7, 481-9
3. Tisato F, Marzano C., Porchia M., Pellei M., Santini C. Med. Res. Rev., 2010, 30, 708-49
4. Pelosi G., Bisceglie F., Bignami F., Ronzi P., Schiavone P, Re M.C., Casoli C., Pilotti E. J. Med. Chem., 2010, 53, 8765-9
5. Yu Y., Kalinowski D.S., Kovacevic Z., Siafakas R.A., Jansson, P.J., Stefani, C., Lovejoy, D.B., Sharpe, P.S., Bernhardt, P.V., Richardson, D.R. J. Med. Chem., 2009, 52, 5271–5294.

Curcumin-based Bifunctional chelators as new diagnostic tools in early diagnosis of Alzheimer's disease.

Giulia Orteca[a], Mattia Asti[b], Sara Rubagotti[b], Michele Iori[b], Pier Cesare Capponi[b], Stefania Croci[b], Zuzana Bednarikova[c], Zuzana Gazova[c], Maria Cristina Menziani[a], Francesco Tavanti[a], Frank Rösch[d], Markus Piel[d], Erika Ferrari[a], Monica Saladini[a]

[a]Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via Campi, 103, 41125 Modena, Italy; [b]Nuclear Medicine Unit, Advanced Technology Department, Santa Maria Nuova Hospital – IRCCS, via Risorgimento 80 42100 Reggio Emilia, Italy; [c]Department of Biophysics, Institute of Experimental Physics, Slovak Academy of Sciences, SK-041 67 Kosice, Slovakia;[d] Institute of Nuclear Chemistry; Fritz-Strassmann-Weg 2 Johannes Gutenberg-University Mainz, D-55128 Mainz, Germany. Email: monica.saladini@unimore.it

Alzheimer's disease (AD) is the most common form of dementia and is characterized by the formation of amyloid plaques, neurofibrillary tangles, and neurotransmitter deficits. Since age, it is the most important risk factor for AD, the rapidly aging population will further increase the number of AD patients, which will have a tremendous impact on society and the medical systems. Although several radio-tracers, especially for positron emission tomography (PET), were developed to study AD *in vivo* (1), the understanding of this disease is far from complete. The accumulation of Aβ aggregates as soluble oligomers and senile plaques in the brain are key indicators of AD, hence, their presence can be exploited as a selective target for diagnostic drugs. Recently, Curcumin has shown to possess *in vitro* and *in vivo* high affinity for Aβ-amyloid plaques (**Fig. 1**) (2), and anti-AD properties due to its ability to bind and subsequently disrupt the aggregation of amyloid peptide and already formed fibrils (3).

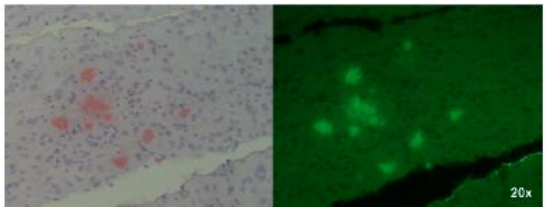


Fig. 1. Micrographs of hippocampal sections (male Tg2576 mice) showing Aβ-amyloid plaques stained with Ga-curcumin complexes (right panels, green) and by Congo Red as comparison (left panels, red) (2).

Radiolabeled curcuminoids could be potential biomarkers for AD by means of nuclear medicine imaging techniques. In the present study, new curcumin derivatives are synthesized and completely characterized. In view of therapeutical applications, their disaggregating ability for aβ fibrillar aggregates was tested, and the most promising compounds were connected through a spacer to a polydentate macrocycle to give new curcumin based bifunctional chelators, to be used as chelating agents to bind radiometals suitable for nuclear medicine applications. If compared with fluorine-18 and technectium-99m, gallium-68 exhibits advantageous features, being a generator produced positron emitter radionuclide with characteristics suitable for diagnostic nuclear medicine and direct labelling of biomolecules (89% β^+, maximum energy = 1.92 MeV; $T_{1/2}$ = 67.7 min). The new chelators were bound to $^{nat/68}$Ga, complexing and labelling conditions were optimized, and complex stability was performed by means of trans-chelation and trans-metallation assays. The results will give insight into the possibility to employ these compounds as radiotracer for monitoring the presence of Aβ-amyloid plaques *in vivo* by positron emission tomography.

References: 1. C. Stains, K. Mondal, I. Ghosh "Molecules that Target beta-Amyloid" ChemMedChem 2 (2007) 1674 (DOI: 10.1002/cmdc.200700140); 2. S. Rubagotti, S. Croci, E. Ferrari, M. Iori, P. C. Capponi, L. Lorenzini, L. Calzà, A. Versari, M. Asti "Affinity of nat/68Ga-Labelled Curcumin and Curcuminoid Complexes for Amyloid Plaques: Towards the Development of New Metal-Curcumin Based Radiotracers" Int. J. Mol. Sci. 17 (2016) 1480; DOI:10.3390/ijms17091480; 3. E. Ferrari, R. Benassi, M. Saladini, G. Orteca, Z. Gazova, K. Siposova "In vitro study

on potential pharmacological activity of curcumin analogues and their copper complexes" Chem Biol Drug Des, 89 (2017) 411 DOI: 10.1111/cbdd.12847.

Synthetic peroxidases for enhancing sensitivity in glucose biosensors

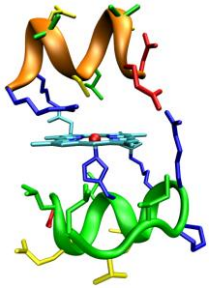
Gerardo Zambrano[a], *Rosa Ester Forgione*[a], *Vincenzo Firpo*[a], *Daniele D'Alonzo*[a], *Flavia Nastri*[a], *Ornella Maglio*[a,b], *Vincenzo Pavone*[c] *and Angela Lombardi*[a]

[a] *Department of Chemical Sciences, University ''Federico II'' of Napoli, Via Cintia 21, 80126, Napoli, Italy;* [b] *IBB-CNR, Via Mezzocannone 16, 80134, Napoli, Italy;* [c]*Department of Biology University of Napoli "Federico II, Via Cintia 26, 80126 Napoli (Italy); email: gerardo.zambrano@unina.it*

In the last decades, research has been focusing on the development of biosensors, based on Glucose oxidase (GOx), for selectively monitoring blood glucose in daily management of diabetes (1). Among active nanomaterials, gold nanoparticles (AuNPs) have been extensively investigated for biosensor application due to their unique physicochemical properties. They indeed represent an efficient loading platform for immobilization of biomolecules (such as proteins, enzymes or DNA). Several studies demonstrated that AuNP-bioconjugates enhance sensitivity and selectivity of optical and electrochemical sensors (2).

Last generation glucose biosensors usually consist in bienzimatic systems, made up of GOx and Horseradish Peroxidase (HRP) as *reporter* enzyme. GOx oxidizes glucose and produce hydrogen peroxide, which in turn undergoes an HRP-mediated reduction, easily detectable electrochemically.

Small-sized synthetic heme-peroxidases represent valuable candidates in biosensor construction. Replacement of HRP (42 kDa) with smaller mimics may enable high sensitivity detection of analytes in samples of different nature, offering economic benefits and high efficiency.


Fe(III)-Mimochrome VIa

Fe(III)-Mimochrome VIa, recently developed by us as HRP mimic, shows higher performances, in terms of reactivity and turnover number respect to the natural enzyme (4).

Here we report the development of a fast and efficient conjugation protocol of GOx and Fe(III)-Mimochrome VIa onto gold surface.

A bioorthogonal approach (Strain Promoted alkyne-azide click chemistry SPAAC) has been selected to ensure fast and quantitative conjugations (5). Preliminary catalytic and quantitative analysis demonstrated that SPAAC-mediated conjugation is more convenient respect to direct enzyme chemisorption onto AuNPs surface. In particular, higher conjugation enzyme/AuNP ratios and initial rate (v_0) were observed. Protocol optimization for the co-immobilization of both enzymes on AuNPs surface is currently being evaluated.

References

1. E.Yoo, S.Lee *Sensors* 10, 4558-4576 (2010).
2. V. Scognamiglio *Biosensors and Bioelectronics* 47, 12-25 (2013).
3. S. Xu, H. Qi, S. Zhou, X. Zhang, C. Zhang, *Microchim Acta* 181, 535-541 (2014).
4. F. Nastri, M. Chino, O. Maglio, A. Bhagi-Damodaran, Y. Lu, Angela Lombardi *Chem. Soc. Rev.* 45, 5020-5054 (2016).
5. E. Sletten, C. Bertozzi *Angew. Chem. Int. Ed.* 48, 6974-6998 (2009).

Metal N-heterocyclic carbenes (NHCs) as antitumor drugs: synthesis and biological activity tests

Federica Guarra[a], Chiara Gabbiani[a], Tarita Biver[a], Natalia Busto[b], Begon˜a García[b]

[a]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy*
[b]*Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s.n., 09001, Burgos, Spain; Email:guarraf@hotmail.it*

Cisplatin and other platinum drugs currently used in the treatment of cancer may have many drawbacks such as systemic toxicity, related resistance and tolerance mechanisms. Therefore, many efforts are being spent in the development of new metal based antitumor drugs. Among these, metal N-heterocyclic carbenes (NHCs) turned out to be particularly promising.(1) NHCs manifest similar donor properties to phosphines, thus affording very stable complexes. In addition, the imidazolium salt precursors are more easily sinthesized than similarly functionalized phosphines.
Herein, we present the synthesis of a series of gold-NHCs and of and silver precursor. These complexes are commonly known to target proteins,(2) yet more recent studies also consider the interaction of gold compounds with dsDNA or G-quadruplexes.(3,4) In particular, our designed complexes aim at combining gold or silver inhibition of TrxR with the intercalating activity of the NHC ligand.(5,6) In this frame, the novel compounds were chemically characterized and different biochemical, biophysical and spectroscopical methods were used to characterize their interaction with target proteins, an oligonucleotide and CT-DNA. Furthermore, preliminary *in vitro* studies on solid tumor cell lines were performed.

References: 1. Oehninger L., Rubbiani R., Ott I., *Dalton Trans, 2013, 42, 3269- 3284*. 2 Alessio E., *Bioinorganic Medicinal Chemistry, Cap. 7, Wiley-VCH* Verlag & Co. KGaA, 20113. 3. Zou T., LumC.T., Lok C-N., Zhanga J-J., Che C-M., *Chem. Soc. Rev., 2015, 44, 8786-8801*. 4. Gratteri P., Massai L., Michelucci E., Rigo R., Messori L., Cinellu M.A.,Musetti,*C.*, Sissi C., Bazzicalupi C., *Dalton Trans., 2015, 44, 3633-3639. Meyer A. et al., ChemMedChem, 2014, 9, 1794-1800.* 6. Citta A., Schuh E., Mohr F., Folda A., Massimino M.L., Bindoli A., Casini A., Rigobello M.P., *Metallomics, 2013, 5, 1006.*

Functionalized Nanopolymers for radiolabeling and medicine applications

Antonella Cartoni[a,b], Iole Venditti[a], Martina Mellace[a], Giovanna Testa[a], Riccardo Faccini[c,d], Carlo Mancini Terracciano[c,d], Elena Solfaroli Camillocci[c,d], Francesco Collamati[d],Silvio Morganti[d], Alessandro Giordano[e], Teresa Scotognella[e], Daria Maccora[e],Massimo Castagnola[f], Federica Marini[f], Dante Rotili[g], Francesca Anna Scaramuzzo[h], Valentina Dini[i], Ilaria Fratoddi[a]

[a] Department of Chemistry, Sapienza University, Rome(IT); [b] CNR-ISM, Rome (IT); [c] Department of Physics, Sapienza University, Rome (IT);[d] INFN, Rome (IT); [e] Institute of Nucleare Medicine, Università Cattolica del Sacro Cuore, Rome (IT); [f] Institute of Biochemistry and Clinical Biochemistry, Università Cattolica del Sacro Cuore, Rome (IT); [g] Department of Chemistry and Technologies of Drugs, Sapienza University, Rome (IT); [h] Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, Via A. Scarpa 14,
00161 Rome (IT); [i] National Centre for Innovative Technologies in Public Health, Istituto Superiore di Sanità Viale Regina Elena, 299 (IT); Email: antonella.cartoni@uniroma1.it

Nanostructured materials have a strong impact on nanomedicine and have attracted more scientific effort due to its scientific and social impact,(1-4) and in particular in nuclear medicine and radiation oncology, both in diagnostic and therapeutic approaches, shows new challenges with new nanomaterials. In fact, radiolabeled nanoparticles are promising tools in cancer diagnosis and therapy.(5-7) Moreover, yttrium-90 (^{90}Y) is a good candidate as suitable β- emitting radioisotope for a new approach to radio-guided surgery (RGS) proposed by some researchers of our group.(8) In this framework, a novel composite nanomaterials, based on poly(methylmethacrylate-co-acrylic acid), P(MMA-co-AA), embedded with yttrium ion ($^{89}Y^{3+}$), were developed as a first step for future production of $^{90}Y^{3+}$ based nanocomposites. The nanoparticles were synthesized by emulsion polymerization technique in the presence of KPS as radical initiator, using different MMA/AA molar ratio in the range 1-20%, DTPA/$^{89}Y^{3+}$ molar ratio 2/1, and different MMA/$^{89}Y^{3+}$ molar ratios, in the range 1-20%. Yttrium doped polymeric nanoparticles were characterized by means of FTIR spectroscopy, DLS and Z-potential measurements, SEM-EDX and AFM (see Fig.1). The DTPA and Y^{3+} influence on morphology and dimension of composite nanoparticles were investigated, and monodispersed nanoparticles with diameters above 30-50 nm were obtained.

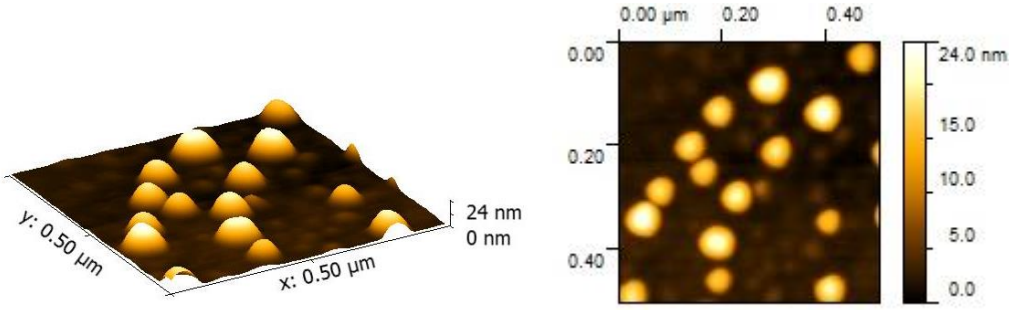


Fig.1. AFM image of P(MMA-co-AA), embedded with DTPA/$^{89}Y^{3+}$

References: 1. I. Ganesh; Renewable and Sustainable Energy Reviews (2016) 59, 1269. 2. I. Venditti, et al., J. Colloids Interf. Sci. (2010) 348, 424. 3. I. Venditti, et al., Sensors and Actuetors B (2007) 126, 35. 4. V. Chenel, et al., J. Nanoparticle Research (2015) 17, 1. 5. V. Rufini, et al., Quarterly Journal of Nuclear Medicine and Molecular Imaging (2013) 57, 122. 6. L. Chronopoulou, et al., New Biotechnology (2016) 33, 23. 7. G. Testa et al., Colloids Surface A (submitted February 2017). 8. M. Marafini, et al., J. Nuclear Medicine (2015) 56, 1501.

Coating with Poly (ε-Caprolactone)-based Hybrid Nanocomposites Synthesized Via Sol-Gel for Improvement of the Titanium Implant Biological Properties

Michelina Catauro[a], *Daniele Naviglio*[b]

[a]*Department of Industrial and Information Engineering, University of Campania "Luigi Vanvitelli", Aversa, Italy;* [b]*Department of Chemical Sciences, University of Naples Federico II, via Cintia 4 –Complesso di Monte S. Angelo 80126 Naples Italy; Email: michelina.catauro@unicampania.it*

In the field of biomaterials, surface modifications of bioinert implants aim to improve their properties (1,2,3). The functional coatings are used to overcome early fail of the metallic implants. The aim of the present study has been to synthesize bioactive and biocompatible silica- and zirconia-based hybrid materials containing poly-ε-caprolactone (PCL) via sol-gel and use these materials to dip coat substrates of commercially pure titanium grade 4 (CP Ti gr. 4) in order to improve their biological properties. ZrO_2/PCL and SiO_2/ PCL inorganic/organic hybrid materials (PCL=6, 12, 24 and 50wt%) were prepared by sol-gel process, using the zirconium propoxide and the titanium butoxide as precursor of ZrO_2 and TiO_2, respectively. Finally, a solution of Poly-ε-caprolactone (PCL) (Mw = 65000) in chloroform was added to the inorganic sol. The materials obtained, in sol phase, were used to coat CP Ti gr.4 substartes by means of the dip coating technique. The ATR-FTIR analysis has been used to study the chemical composition of the obtained coatings. Each spectrum has confirmed the formation of hydrogen bonds between the organic and inorganic phases. SEM micrographs of all coatings has shown the cracks formation, that decreased when polymer was added to the matrix and crack-free films were obtained using high PCL amounts (Figure 1(b, d)). Moreover, the apatite deposition on sample surfaces is clearly visible in SEM images recorded after SBF test. Irrespective of the matrix and PCL amount, the whole surface of all coated samples is covered by a globular precipitate and the EDS confirms that the observed layer is composed of calcium and phosphate. On the contrary, fewer globules are visible on the surface of the uncoated sample. WST-8 assay shows that the highest values of cell viability were obtained using coatings PCL-free o containing PCL 6wt%. This result can be explained by the hydrophobic nature of PCL which inhibits cells adhesion and consequently causes a decrease of cells vitality. In conclusion, the coating presence improves the bioactivity and biocompatibility of the CP Ti grade 4, especially if low amount of PCL are contained in a silica matrix. However, the PCL is necessary to obtain crack-free coatings.

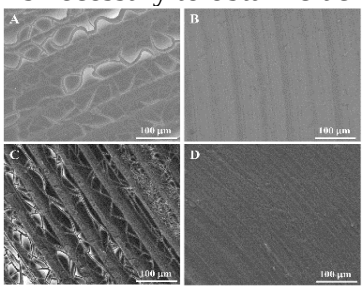


FIGURE 1. SEM of (a) SiO_2, (b) SiO_2+50%PCL (c) ZrO_2 and (d) ZrO_2+50%PCL hybrid coatings

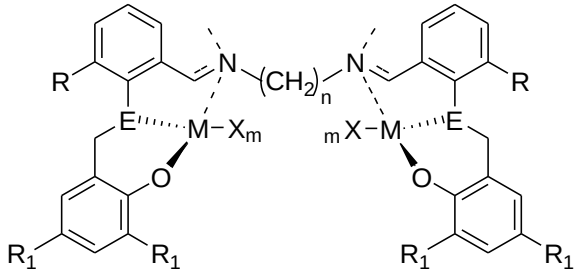
References: 1. Catauro, M., et al. Materials Science and Engineering C, 2014. 43: p. 375-382. 2.Catauro, M., et al. Journal of Sol-Gel Science and Technology, 2015. 76(2): p. 241-250. 3.Wang, D. and G.P. Bierwagen. Progress in Organic Coatings, 2009. 64(4): p. 327-338.

Fixation of Carbon Dioxide in Organic Carbonates Catalyzed by Bimetallic Complexes

Mariachiara Cozzolino, Flavia Melchionno, Mina Mazzeo, Claudio Pellecchia, Marina Lamberti

Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 84084-Fisciano, Italy; E-mail: macozzolino@unisa.it

Carbon dioxide is an attractive, renewable one-carbon source: it is non toxic, highly abundant, relatively inexpensive, however its thermodynamic stability is the major impediment to its utilization. For this reason feasible reactions, in combination with the CO_2, involve highly reactive chemicals, such as epoxides (1). In particular, the transformation of epoxides and carbon dioxide into either aliphatic polycarbonates or cyclic carbonates is of commercial importance. Aliphatic polycarbonates produced by these reactions have been commercialized as adhesive, binders and coatings (2). In the same way, cyclic carbonates have numerous and interesting applications since they can be used as polar aprotic solvents, electrolytes in lithium ion batteries and intermediates in organic synthesis (3). Several metal-based catalytic systems for this reaction have been developed and in most cases dinuclear catalysts show enhanced performances compared to their related mononuclear analogues (4). For this reason in this work we decided to prepare new hexadentate dianionic ligands which will be able to host two different metallic centres (Figure 1). The new ligands scaffold allows to vary the nature of the nitrogen donors atoms (amine and imine), the substituents on the aromatic rings, and to modulate the length of the bridge in order to find the optimal distance for the cooperation between the two metallic centers. We concentrate on common metals which are either non-toxic, inexpensive, earth-crust abundant, such as iron, zinc and magnesium. The new bimetallic complexes have been employed as catalysts for CO_2/epoxide reactions, evaluating the effect of the reaction conditions (nature of epoxide, temperature, pressure of CO_2) on the productivity and selectivity of the catalytic systems.



M= Mg, Zn, Fe
X= alkoxy, alkyl, acetate, halogens groups
E= S, O
R= H, CH_3, Cl
R_1= CH_3, ^{t}Bu

Figure 1. Bimetallic complexes bearing new hexadentate dianionic ligands.

References: 1. M. Aresta, A. Dibenedetto, A. Angelini, Chem. Rev. **114**, 1709-1742, (2014). 2. M. Taherimehr, P. P. Pescarmona, J. Appl. Polym. Sci. **131**, 41141-41158, (2014). 3. J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, Green Chem. **17**, 1966-1987, (2015). 4. G. W. Coates, D. R. Moore, Angew. Chem., Int. Ed. **43**, 6618-6639 (2004).

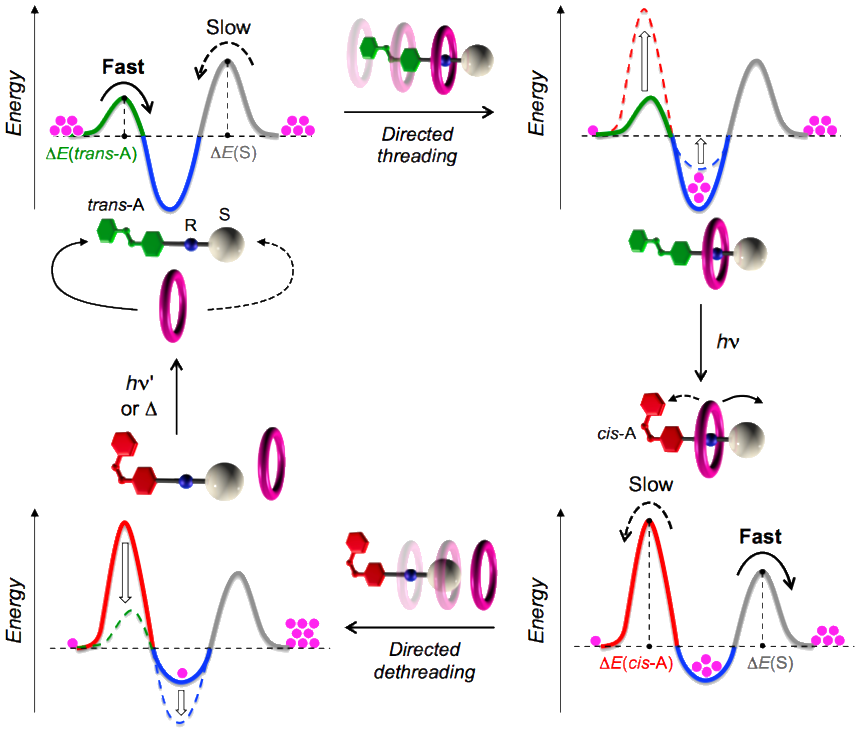
Autonomous supramolecular pumps fueled by light

Alberto Credi[a], Massimo Baroncini[a], Lorenzo Casimiro[a,b], Christiaan de Vet[a], Jessica Groppi[a], Marcello La Rosa[a], Serena Silvi[a,b]

[a] CLAN - Center for Light Activated Nanostructures, Università di Bologna and Istituto ISOF-CNR, via Gobetti 101, 40129 Bologna [b] Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna; alberto.credi@unibo.it

The bottom-up design, preparation and characterization of chemical systems that behave as molecular-scale machines and motors is a stimulating challenge of nanoscience (1). The interest on this kind of systems arises from their ability to perform a (useful) function in response to chemical and/or physical signals. In this context, the use of light stimulation has several advantages, primarily because photons can be used to supply energy to the system (i.e., write) and to gain information about its state (i.e., read) (2).

Here we will describe investigations undertaken in our laboratories aimed at photo-inducing and -controlling large-amplitude molecular motions, both under thermodynamic and kinetic viewpoints, in threaded and interlocked multicomponent (supramolecular) species that comprise photoreactive units (3,4,5,6,7). This work has culminated with the design, construction and operation of a system in which light irradiation causes the relative unidirectional transit of a nonsymmetric molecular axle through a macrocycle (see Figure) (8).



As a matter of fact, this is the first example of a photochemically driven artificial molecular pump (9,10). Systems of this kind can not only lead to radically new approaches in catalysis, materials science and medicine, but also disclose unconventional routes for the conversion of light energy into chemical energy. Such applications are being investigated in the frame of the project LEAPS-Light effected autonomous molecular pumps: towards molecular transporters and actuating materials, funded by the European Research Council (Advanced Grant n. 692981).

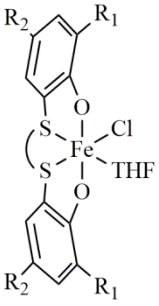
References: 1. V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines – Concepts and Perspectives for the Nano World*, Wiley-VCH, Weinheim, 2008. 2. P. Ceroni, A. Credi, M. Venturi, *Chem. Soc. Rev.* **2014**, *43*, 4068. 3. T. Avellini et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 1611. 4. M. Baroncini, S. Silvi, M. Venturi, A. Credi, *Angew. Chem. Int. Ed.* **2012**, *51*, 4223. 5. A. Arduini et al., *J. Am. Chem. Soc.* **2013**, *135*, 9924. 6. V. Fasano et al., *J. Am. Chem. Soc.* **2014**, *136*, 14245. 7. G. Ragazzon, B. Colasson, A. Credi, *Chem. Eur. J.* **2017**, *23*, 2149. 8. G. Ragazzon, M. Baroncini, S. Silvi, M. Venturi, A. Credi, *Nat. Nanotech.* **2015**, *10*, 70. 9. E. Sevick, *Nat. Nanotech.* **2015**, *10*, 18. 10. G. Ragazzon, M. Baroncini, S. Silvi, M. Venturi, A. Credi, *Beilstein J. Nanotech.* **2015**, *6*, 2096.

Reaction of CO_2 with Epoxides Promoted by [OSSO]-type Fe(III) Complexes

Francesco Della Monica[a,b], *Sai V. C. Vummaleti*[c], *Antonio Buonerba*[a,b], *Assunta De Nisi*[d], *Magda Monari*[d], *Stefano Milione*[a,b], *Alfonso Grassi*[a,b], *Luigi Cavallo*[c], *Carmine Capacchione*[a,b]

[a] *Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italia;* [b] *CIRCC, Interuniversity Consortium Chemical Reactivity and Catalysis, via Celso Ulpiani 27, 70126 Bari, Italia;* [c] *KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Arabia Saudita;* [d] *Dipartimento di Chimica G. Ciamician, Alma Mater Studiorum, Università di Bologna, via Selmi 2, Bologna, Italia; email: fdellamonica@unisa.it*

The suppression of carbon dioxide emission from anthropic activities is a hard, but mandatory, objective to reach worldwide. The reuse of carbon dioxide itself for the synthesis of chemicals, represent a valid strategy for the reduction of its concentration in the atmosphere.(1) One of the most interesting processes studied for this purpose is the reaction of CO_2 with epoxides for the synthesis of cyclic organic carbonates (COCs) and polycarbonates (PCs).(2) Recently we reported on a series of dinuclear Fe(III) complexes, based on thioeter-tri-phenolate ligands, that resulted to be efficient catalysts for the selective synthesis of COCs.(3) To better understand the effect of nuclearity on the catalytic activity, saving the presence of sulfur neutral donor in the coordination sphere of the iron centre, we prepared a group of [OSSO]-type Fe(III) mononuclear complexes (Figure 1).



1-4

n	⌒	R_1	R_2
1	$(CH_2)_2$	CH_3	CPh_3
2	$(CH_2)_2$	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$
3	$(CH_2)_2$	CH_3	CH_3
4	*c*-Hex	$C(CH_3)_3$	$C(CH_3)_3$

Figure 9. [OSSO]-type Fe(III) comlexes **1**-**4**.

The use of complexes **1**-**4**, in the presence of a suitable co-catalyst, under mild reaction conditions is described in this contribution. In particular the binary catalytic system is able to selectively produce COCs when the starting reactant is an acyclic epoxide while PC is obtained if the starting epoxide is cyclohexene oxide. A DFT study was carried out to better understand the role of the metal centre in the reaction pathway.

References: 1. Martens J. A., Bogaerts A., De Kimpe N., Jacobs P. A., Marin G. B., Rabaey K., Saeys M., Verhelst S., *ChemSusChem* **2017**, *10*, 1039-1055. 2. C. Martìn, G. Fiorani, A. W. Kleij, *ACS Catal*. **2015**, *5*, 1353-1370. 3. Della Monica, F.; Vummaleti, S.V.C.; Buonerba, A.; De Nisi, A; Monari, M.; Milione, S.; Grassi, A.; Cavallo, L.; Capacchione, C.; *Adv. Synth. Catal*. **2016**, *358*, 3231-3243.

Synthesis and thermal behavior of Sn-based lead-free nanosolders

Simona Delsante,[a,b] Gabriella Borzone[a,b], Rada Novakovic[b]

[a]Department of Chemistry and Industrial Chemistry, Genoa University, INSTM-UdR Consortium, Via Dodecaneso 31, 16146 Genoa, Italy; [b]Institute of Condensed Matter Chemistry and Energy Technologies, National Research Council (ICMATE-CNR), via de Marini 6, 16149 Genoa, Italy

The potential applications of nanoalloys in different fields originates the interest in obtaining reliable thermodynamic data necessary to determine the stability of the nanoalloy systems, to develop materials property databases, as well as to carry out theoretical calculations to substantiate experimental work (1, 2). The resolution to ban the use of solders containing Pb in all new electronic devices raised considerable interest in the field of low temperature interconnect technologies and materials, mainly based on Sn incorporating Ag, Cu and sometimes Bi, Zn and other metals in varying amounts (3). The melting point of most lead-free solders is higher than the widely Sn-Pb solder (melting point 183°C) adopted in electronic devices in the past. Owing to the large surface to volume ratio and size effect, in particular concerning the melting point depression, the metallic nanoparticles (NPs), have gained an increasing attention for their application in the field of the lead-free solders (4).

In the present study AgSn and SnAgCu (SAC) nanoparticles at the eutectic composition have been successfully synthesized by a low temperature chemical reduction method. The thermodynamic characteristics of the nanocrystals have been investigated by means of differential scanning calorimetry (DSC). X-ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM and FE-SEM) have been employed to study the morphology, microstructure and phase evolution of the as-synthesized particles before and after heating process. The formation of the phases pertaining to the binary and ternary eutectics has been confirmed by XRD analysis, and a depression melting temperature of 7-10°C was observed for both systems. The experimental results will be discussed and compared with the corresponding literature data.

1. R. Ferrando, J.Jellinek,R.L. Johnston, Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles, Chem. Rev. 108 (2008) 845- 910
2. G. Borzone, S. Delsante, in “Handbook of High-Temperature Lead-Free Solders, Thermodynamic Properties” and] R. Novakovic, Yu. Plevachuk “Thermophysical Properties”, Volume 2, WG1 Materials Properties, Ed. A. Watson, Brno, Czech Republic, COST office, Brussels, Belgium, pp. 7-141, 2012, ISBN: 978-80-905363-2-6.
3. D. Giuranno, S. Delsante, G. Borzone, R. Novakovic, Effects of Sb addition on the properties of Sn-Ag-Cu/(Cu, Ni) solder systems, J Alloys Compd. 689 (2016) 918-930.
4. J. Wu, S-b Xue, J-W Wang, S. Liu, Yi-L. Han, Liu-J. Wang, Recent progress of Sn–Ag–Cu lead-free solders bearing alloy elements and nanoparticles in electronic packaging, J Mater Sci: Mater Electron, 27 (2016) 12729–12763

Energy efficient production of hydrocarbons and formate by depolarized-anode CO_2 electroreduction on tailored copper nanostructures

Jonathan Filippi[a], *Manuela Bevilacqua*[a], *Marco Bellini*[a], *Maria Folliero*[a,b], *Andrea Marchionni*[a], *Hamish A. Miller*[a], *Maria Pagliaro*[a,b], *Francesco Vizza*[a]

[a] *Institute of Chemistry of Organometallic Compounds (ICCOM) National Research Council (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, FI (Italy);* [b] *Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via Aldo Moro 2 53100 Siena, SI (Italy); jonathan.filippi@iccom.cnr.it*

The electroreduction of carbon dioxide is a promising candidate for promoting high energy density storage processes and providing alternative preparation routes for fuels, energy vectors, and chemicals. On the other hand, the electrochemical reduction of CO_2 is an energy-intensive process, both on thermodynamic and kinetic point of view, requiring extensive studies on electrocatalytic structures. Copper-based electrocatalysts have the almost unique characteristic to reduce carbon dioxide to C1-C3 hydrocarbons and alcohols but the activities and stabilities are rather low (1). Modifications of the copper surface as well as alloying can potentially improve the electrocatalytic performance; furthermore the face index of the electrocatalyst have a huge effect on selectivity (2,3). In this study, plain metallic copper is modified by additive (copper electrodeposition) and subtractive (electrochemical faceting) roughening and structure and performance of those materials is evaluated by material investigation and product analysis in a alkaline membrane electrolizer, demonstrating the possibility of driving the selectivity towards hydrocarbons or formate depending on the type of electrochemical roughening treatment applied. In particular, it was observed that the electrochemical faceting on copper drove the selectivity towards methane while increasing the total faradaic efficiency compared to plain polycrystalline copper surface. The electrodeposited copper sample maintained almost the same selectivity of the plain copper, instead, but with higher total faradaic efficiency. In addition the electrochemical reduction of carbon dioxide at the cathode is coupled with (bio)alcohol selective (4) partial oxidation at the anode, leading to a reduction of the electrical requirements of the reaction and opening a route for the production of acetate from ethanol (4). The total cell potentials for carbon dioxide electrolysis when using sacrificial (bio)ethanol ranges from 1.6 to 1.8V, compared to almost 4V when a state-of-the-art water-splitting anode is employed. The energy consumption of the entire system, assessing the ethanol energy cost at an ERoEI (Energy Return on Energy Invested) value of 8 is almost half of the traditional CO_2 electrolysis cell with a total energy efficiency of 50%.

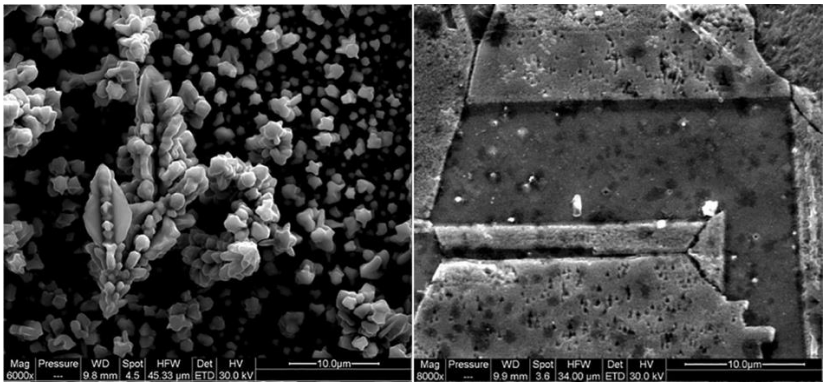


Figure 1: left: SEM micrographs of Cu electrodeposits generated by EP process on a Cu foil surface and right: SEM micrographs of surface defects generated by ECF on a Cu foil surface (Conditions: f=0.25 Hz; 15 h)

References: 1. Y. Hori, I. Takahashi, O. Koga, N. Hoshi, J. Phys. Chem. B 2002, 106, 15– 17. 2. R. Reske, M. Duca, M. Oezlasan, K. J. P. Schouten, M. T. M. Koper, P. Strasser, J. Phys. Chem. Lett. 2013, 4, 2410 – 241. 3. Y. Hori, I. Takahashi, O. Koga, N. Hoshi, J. Mol. Catal. A 2003, 199, 39– 47. 4. M. Bevilacqua, J. Filippi, A. Lavacchi, A. Marchionni, H. A. Miller, W. Oberhauser, E. Vesselli, F. Vizza, Energy Technol. 2014, 2, 522 – 525.

Preparation of novel hydrophobic cellulosic composites containing Silver (I) acylpyrazolonato

Eugenia Giorno*[a], Alessandra Crispini[ab] , Iolinda Aiello[ab], Nicolas Godbert[ab], Massimo La Deda[ab], Fabio Marchetti[c], Claudio Pettinari [cd], Riccardo Berardi[e], Pasquale Alfano[e]

*[a]MAT-INLAB (Laboratorio di Materiali Molecolari Inorganici, Dipartimento di Chimica e Tecnologie Chimiche, 87036 Rende (CS), Italia ; [b] CNR NANOTEC- Istituto di Nanotecnologia U.O.S Cosenza, 87036 Rende (CS), Italia; [c] Scuola di Scienze e Tecnologie, Scola di farmacia, Divisione di Chimica, Università degli Studi di Camerino, Via S. Agostino 1, 62032 Camerino (MC), Italia; [d] ICCOM, CNR 62032 Camerino, Italia; [e] TIFQLAB s.r.l Via Danimarca 87036 Rende (CS), Italia;

The surface modification of cellulose is central for a fast growing area of applications, since most vegetable-derived natural polymers are renewable materials, some of them displaying properties comparable to those of petroleum derived products.(1) The preparation of highly hydrophobic cellulose based materials is particularly important in the field of food packaging. Most materials used for food packaging applications are still produced from fossil fuels, so non-renewable and also nearly non-biodegradable, therefore representing an environmental problem.(2) In order to prepare hydrophobic cellulose, the hydroxyl groups are chemically modified, due to their reactive nature compared to the rest of the molecule. To date, fluorochemicals are usually employed for this purpose. These compounds impart not only hydrophobicity, but also oil and stain repellency.(3) However, longer fluoroalkyl chains have bio-accumulative potential in living organisms since their tendency to oxidation towards highly persistent pollutants.(4) For this reason, in this work, an alternative to the already existing processes for the preparation of hydrophobic cellulose is provided. Novel composite materials based on cellulose and Silver(I) acylpirazolonato complexes have been prepared for this aim. Since Silver (I)-based compounds are highly toxic to microorganisms, as proved recently by a class of new complexes based on acylpyrazolone synthesized and tested on some antibacterial family.(5) In this work, pure and functionalized cellulose are used as substrate for the deposition of silver complexes obtained through coordination with different acylpirazolonato ligands able to promote both covalent chemical bonds and/or van der Waals interactions with the substrate. These ligands are chosen in order to facilitate the interaction of the resulting complexes with the hydroxyl groups on the cellulose surface. Once the cellulose composites containing Silver(I) acylpyrazolonato are obtained, the hydrophobicity of this modified cellulose is going to be evaluated by many different methodologies, also addressed to control the stability, biodegradability and biocompatibility of the new synthesized silver-based composites.

References: 1. Reference n. 1 Yidong Zhong, Anil N. Netravali, 'Green' surface treatment for water-repellent cotton fabrics, ***Surface Innovations***, 2016 . 2. Reference n.2 HMC Azeredo, MF Rosa, LHC Mattoso, Nanocellulose in bio-based food packaging applications, *Industrial Crops and Products*, 2017. 3. Reference n.3 X**.** Zen, J**.**Gong, Y**.** Deng, Water resistance improvement of paper by superhydrophobic modification with microsized $CaCO_3$ and fatty acid coating, ***Colloids and Surfaces A: Physicochem. Eng. Aspects,*** 2009. 4. Reference n. 4 S.H. Li, J.Y. Huang, M.Z. Ge, S.W. Li, T.L. Xing, G.Q. Chena, Y.Q. Liu, K.Q. Zhang, S.S. Al-Dey, Y.K. Lai, Controlled grafting superhydrophobic cellulose surface with environmentally-friendly short fluoroalkyl chains by ATRP, ***Materials and Design***, 2015. 5. Reference n. 5 F. Marchetti, J. Palmucci, C. Pettinari, R. Pettinari, S. Scuri, I. Grappasonni, M. Cocchioni, M. Amati, F.Lelj, A. Crispini , Linkage Isomerism in Silver Acylpyrazolonato Complexes and Correlation with Their Antibacterial Activity, ***Inorg. Chem***., 2016.

Improved size-tunable synthesis of gold nanorods and surface functionalization strategies for biomedical applications

Vincenzo Mangini[a] *and Roberto Fiammengo*[a]

[a] *Center for Biomolecular Nanotechnologies@UniLe, Istituto Italiano di Tecnologia (IIT),Via Barsanti, 73010 Arnesano, Lecce, Italy*
E-mail: vincenzo.mangini@iit.it

Gold nanorods (AuNRs) are attracting interest for biomedical applications due to their unique optical and electronic properties which are dependent on their shape and size. Compared to spherical nanoparticles, AuNRs possess a strong adsorption band in the near-infrared region of the electromagnetic spectrum. Since biological tissues show minimal light adsorption in this spectral region, AuNRs may additionally allow the investigation of nanoparticle targeting(1) and biodistribution via tissue imaging(2) using near-infrared light. The most common method to produce AuNRs is seed-mediated synthesis involving the use of cetyltrimethylammonium bromide (CTAB) to control aspect ratio.(3) Nevertheless, CTAB is known to be highly cytotoxic.(4) It tightly adsorbs on the AuNR surface and it is difficult to be removed without causing aggregation. Yet, the ability to completely remove CTAB while maintaining colloidal stability are key requirements for AuNR application in vivo.

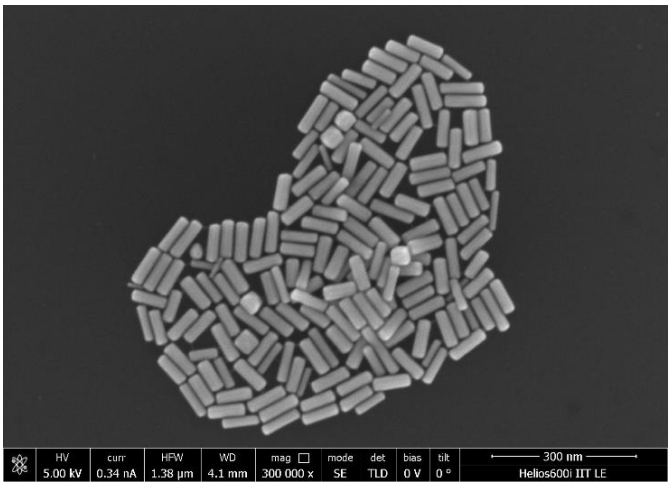


Figure: SEM micrograph of PEGylated AuNRs

In this contribution, we describe the improved synthesis of monodisperse AuNRs with different aspect ratio and the optimization of surface functionalization strategies to replace CTAB with biocompatible surface modifiers such as ω-functionalized PEG-thiols developed in our group.(5) We report the physicochemical characterization of these systems and demonstrate that the PEG-based passivation layer allows to fully abolish cytotoxicity. We finally show that mixed self-assembled monolayers of ω-functionalized PEG-thiols can be exploited for simple conjugation of a precise number of biologically active molecules onto the AuNRs. We envision a great potential for these functionalized AuNRs as safe nanomaterials for biomedical applications.

References:
1. Huang, X. H.; El-Sayed, I. H.; Qian, W.; El-Sayed, M. A., J. Am. Chem. Soc. 2006, 128 (6), 2115-2120.
2. Wang, S. W.; Xi, W.; Cai, F. H., et al., Theranostics 2015, 5 (3), 251-266.
3. Nikoobakht, B.; El-Sayed, M. A., Chem. Mater. 2003, 15 (10), 1957-1962.
4. Wang, L. M.; Liu, Y.; Li, W., et al., Nano Lett. 2011, 11 (2), 772-780.
5. Maus, L.; Dick, O.; Bading, H.; Spatz, J. P.; Fiammengo, R., ACS Nano 2010, 4 (11), 6617-6628.

Functional dipyrrins for a multi- purpose task: chemical sensing and energy transfer investigations

Mariachiara Trapani[a], *Massimiliano Cordaro*[b,c], *Andreea Militaru*[a], *Andrea Romeo*[a,b], *Elisabetta Collini*[d], *Maria Angela Castriciano*[a], *Luigi Monsù Scolaro*[a,b]

[a] *CNR- ISMN, Istituto per lo Studio dei Materiali Nanostrutturati c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy;*
[b] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy;* [c] *CNR- ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Messina;* [d] *Dipartimento. di Scienze Chimiche, Via Marzolo 1, 35100 Padova, Italy*
trapani@mail.pa.ismn.cnr.it

The synthesis of multifunctional π-electron systems with specific photophysical properties represents a goal for researchers both in synthetic chemistry and materials science. In this framework, opportunely functionalized chromophores like porphyrins or bodipys can be considered high versatile tools for multifunctional applications such as artificial light harvesting supramolecular architectures or as chemical sensors for the detection of contaminants in solution. Despite many reports dealing with the use of porphyrin or bodipy systems, their subunits such as dipyrrin are only rarely used for photometric metal detection (1). Indeed, these classes of molecules due to their photophysical properties and for their high coordination constants with metal ions and then their optical feedback upon coordination, are excellent candidate for achieving new fast, cheap and sensitive chemical sensors. Based on these considerations, recently we focused our attention on the synthesis of new molecules opportunely functionalized with uracil and/or the acetylated diamino pyridine moieties for detection of contaminant such as melamine and/or metal ions in solution. The spectroscopic investigation has been carried out using a combination of UV/Vis absorption, static and time- resolved fluorescence, and ^{1}H- NMR. Furthermore, in the case of bodipy molecules, the presence of the two complementary groups able to interact by hydrogen bonding allow the formation of an heterodimer that could be an interesting system to investigate the role and the mechanism of long- lived quantum coherence phenomenon in electronic energy transfer (EET) in artificial photosynthetic light harvesting systems (LHs) (2, 3,4).

References: 1. S. Guski, M. Albrecht, T. Willms, M. Albrecht, T. Nabeshima, F. Pan, R. Puttreddy, K. Rissanen, *Chem. Comm.*, 2017, 53, 3213- 3215. 2. E. Collini, C. Y. Wong, K. E. Wilk, P. M. G. Curmi, P. Brumer, G. D. Scholes, *Nature*, **2010**, 463, 644- 648. 3. E. Collini, G. D. Scholes, *Science*, **2009**, 323, 369- 373. 4. D. Hayes, G.B. Griffin, G. S. Engel, *Science*, **2013**, 340, 1431-14

Ring Opening Metathesis Polymerization promoted by ruthenium benzylidene complexes with unsymmetrical NHC ligands

Veronica Paradiso, *Fabia Grisi*

Università degli Studi di Salerno, Via Giovanni Paolo II 50, 84084 Fisciano (SA)
vparadiso@unisa.it

Olefin Metathesis is one of the most important catalytic transformations for the formation of carbon-carbon double bonds.(1) The metathesis reaction involving the polymerization of cyclic unsaturated monomers is known as ROMP (Ring Opening Metathesis Polymerization) and is nowadays implicated in the production of several industially important polymers, such as Norsorex and Vestenamer.(2)
Due to their non-symmetric nature, Grubbs second generation catalysts bearing unsymmetrical N-heterocycle carbene (u-NHC) ligands are particularly efficient in the copolymerization of norbornene (NBE) with cys-cyclooctene (COE) and cyclopentene (CPE).(3)
Recently in our group new u-NHC ruthenium catalysts **1** and **2** have been synthesized (**figure 1**). These catalysts, bearing two phenyl groups with syn or anti configuration on backbone positions, have been investigated in several metathesis transformations, showing valuable activity and selectivity.(4) Moreover these two isomers have exhibited a very different catalytic behavior, thus demonstrating the important role of backbone configuration also for u-NHC ruthenium catalysts, according to the literature regarding other families of metathesis catalysts.(5)

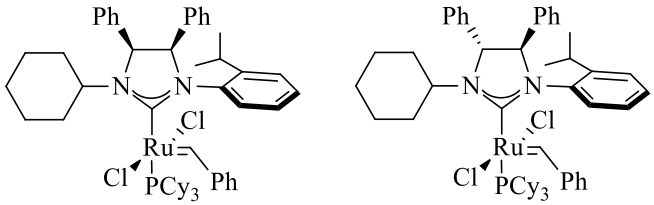


Figure 1: Ruthenium catalysts with backbone substituted u-NHC ligands

In this contribution we discuss the reactivity of **1** and **2** in the copolymerization of NBE with CPE and COE. This represents nowadays a very challenging scope, being the copolymerization promoted by backbone substituted u-NHC catalysts still totally unexplored.

References: 1. *Olefin Metathesis: Theory and Practice.* Ed. K. Grela, **2014**, Wiley. 2. a) K. Weissermel, H. J. Harpe, *Industrial Organic Chemistry*, 3rd ed., **2008** Wiley; b) M. Schuster, S. Blechert, *Angew. Chem. Int. Ed.* **1997**, 36, 2036. 3. K. Vehlow, D. Wang, M. Buchmeiser, S. Blechert, *Angew. Chem. Int. Ed.* **2008**, *47*, 2615. 4. a) V. Paradiso, V. Bertolasi, F. Grisi, *Organometallics* **2014**, *33*, 5932; b) V. Paradiso, V. Bertolasi, C. Costabile, F. Grisi, *Dalton Trans.* **2016**, *45*, 561. 5. V. Paradiso, C. Costabile, F. Grisi, Molecules **2016,** 21, 117.

Laser treatment of tattoo pigment PG-36

Elvira Maria Bauer[a], Simonetta Antonaroli[b], Emanuele Scibetta[b],Susanna Piccirillo[b], Marilena Carbone[b]

[a] Istituto di Struttura della Materia del Consiglio Nazionale delle Ricerche (ISM-CNR), RM 1, Via Salaria km 29.3, 00015 Monterotondo, Italy; [b] Department of Chemical Sciences and Technologies, University of Rome "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Rome, Italy

Worldwide, tattooed population has been significantly increasing for a long time, especially among young people (1). To date, because of an improved self-image or social stigmatization, we simultaneously observe the opposite tendency: many tattooed individuals undergo a therapy of tattoo removal, the most common removal pathway being treatment with Q-Switch laser. In spite of this, few though remarkable investigations have been carried out aimed at understanding the tattoo inks decomposition patterns (2-3). Inks are typically made of two components: the pigment and the vehicle. In the present study, we investigate the chemical processes, and the morphological changes following the laser and ultrasound treatment of the pigment commercially known as PG36, a fully halogenated copper-phtalocyanate, with formula $C_{32}H_{16}Br_6Cl_{10}N_8Cu$ (Fig. 1a) which imparts yellowish green color to some of the most common inks on the market. Laser treatments were carried out with a Nd:YAG laser, operating at 532 nm, with a fluence of 50 mJ/mm^2, on two different dispersions of the pigment, i.e. in isopropanol and in water. The decomposition fragments were, then, analyzed by GC-mass. The morphology variations were monitored by Scanning Electron Microscopy. In Fig. 1b) and c) the SEM micrographs are reported before and after 30 minutes sonication of the pigment with

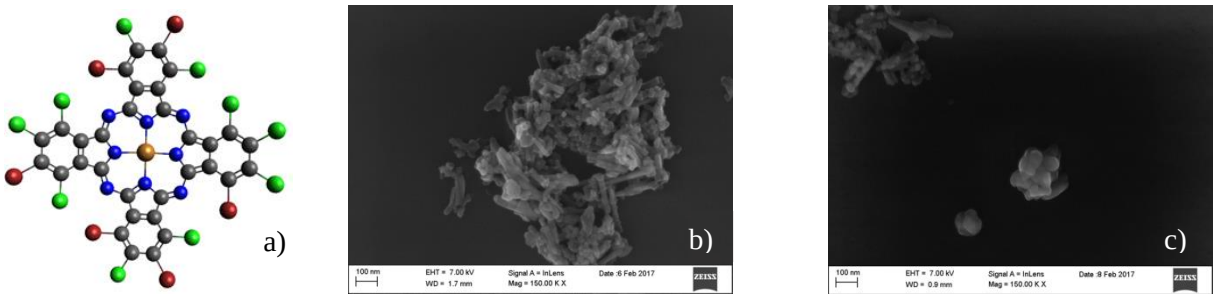


Fig.1 a) Scheme of the phtalocyanine in PG36, the green balls represent Br atoms, the red ones, chlorine, gray ones carbon, the blue ones nitrogen and the central bronze ball is the Cu central metal. SEM micrograph of b) PG36 at 150Kx magnification; c) PG36 after 30 minutes sonication at 130 Watt, 12 KHz and 60% wave amplitude at the same magnification.

The ultrasound treatment, change the morphology from the typical β arrangement of the phtalocyanine aggregates to roundish agglomerates. The rearranged compound still contain Br and Cl, though it cannot be inferred whether a fragmentation occurred.
We found out that the laser treatment yields very complex fragmentation patterns, which include the generation of toxic fragments such as BrCN and ClCN, regardless of the dispersion solvent.

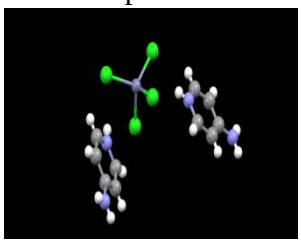
References:
1. A.E Laumann, A.J. Derick, "Tattoos and body piercings in the United States: a national data set", *J. Am. Acad. Dermatol*. 2006, 55, 413.
2. I. Schreiver, C. Hutzler, P. Laux, H.P. Berlien, A. Luch, "Formation of highly toxic hydrogen cyanide upon ruby laser irradiation of the tattoo pigment phthalocyanine blue", *Nature Scientific Reports*, 2015, 12915.
3. I. Schreiver, C. Hutzler, S. Andree, P. Laux, A. Luch, " Identification and hazard prediction of tattoo pigments by means of pyrolysis-gas chromatography/mass spectrometry", *Arch. Toxicol.*, 2016, 90,1639-1650.

Analysis of molecular structure, spectroscopic properties (FT-IR, micro-Raman and UV–vis) and quantum chemical calculations of free and ligand 4 amino pyridine acid in metal halides (Zn, Hg and Cd)

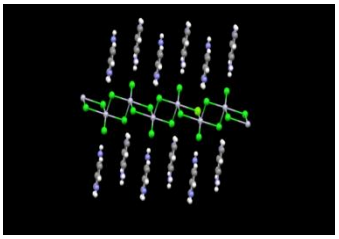
Rim Ben debabis [a], *G. Bruno* [b] *and Fatma Zouari* [a]

[a] *Laboratory of Materials and Environmental Sciences, University of Sfax, BP 1171, 3000, Sfax, Tunisia.*
[b] *Department of Chemical, Biological, Pharmaceutical, and Environmental Sciences Viale Ferdinando. Stagno D'Alcontres, 31 98166 Messina, Italy*
E-mail address: rim.bedbabis@yahoo.fr

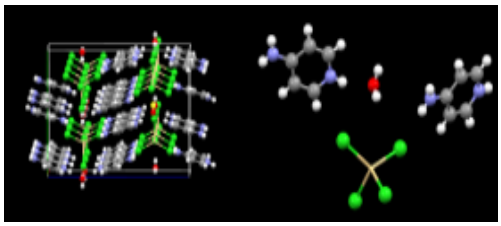
Organic-inorganic hybrid compounds have paid more and more attention in the solid-state materials chemistry due to their significant applications in the field of optics, ionics, mechanics, energy, environment, biology and medicine. Those applications include a new generation of photovoltaic and fuel cells, photo-catalysts, sensors, functional smart coatings, smart membranes and separation devices, micro-optical and photonic components. Especially the materials based to halogenated metals such as Zn, Hg, and Cd, etc... present very interesting physical properties (1,2,3) and these materials show good results due to their electronic properties and extended structure, with strong interaction between the atoms, ions or molecules which occur throughout the lattice system.
In this study we report the synthesis of a series of novel organic inorganic hybrid compound $(C_5H_7N_2)_2MCl_4$ (M = Zn, Hg, Cd). The crystal structure, vibrational, and optical properties were characterized by X-ray diffraction (XRD), Raman and infrared spectroscopy, UV–vis absorption studies, the structural properties and vibrational frequencies have been investigated extensively using density functional theory (DFT). We will explain more about crystal packing and hydrogen bonds in these compounds in details.



$(C_5H_7N_2)_2ZnCl_4$



Packing of $(C_5H_7N_2)_2HgCl_4$



Packing of $(C_5H_7N_2)_2CdCl_4$

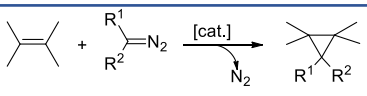
References
1. M.S. Ski, A. Katrusiak, J. Phys. Rev. B 73 (2006) 134–111.
2. L.D. Carlos, R.A. Sa Ferreira, V. de Zea Bermudez, S.J.L. Ribeiro, J. Adv. Funct. Mater. 2 (2001) 111.
3. Y. Kato, D. Ichii, K. Ohashi, H. Kunugita, K. Ema, K. Tanaka, T. Takahashi, T.Kondo, J. Solid State Commun. 128

Iron Porphyrin Amino Ester Conjugates: new 'Totem' Porphyrin Catalysts.

Daniela M. Carminati[a], Daniela Intrieri[a], Stephane Le Gac[b], Thierry Roisnel[b], Bernard Boitrel[b], Lucio Toma[c], Laura Legnani [c] and Emma Gallo[a].

[a]Department of Chemistry, University of Milan. Via C. Golgi 19, 20133 Milan (Italy); [b]Institut des Sciences Chimiques de Rennes, Université de Rennes 1. 263 Avenue du Général Leclerc, 35042 Rennes Cedex (France); [c]Department of Chemistry, University of Pavia. Via Taramelli 12, 27100 Pavia (Italy); daniela.carminati@unimi.it.

Cyclopropane containing compounds represent a class of very active molecules which often display biological and pharmaceutical characteristics (1,2). One of the most sustainable and atom-efficient methodologies to synthesise cyclopropanes is the one pot reaction of diazo compounds with alkenes forming N_2 as the only stoichiometric by-product (Scheme 1).



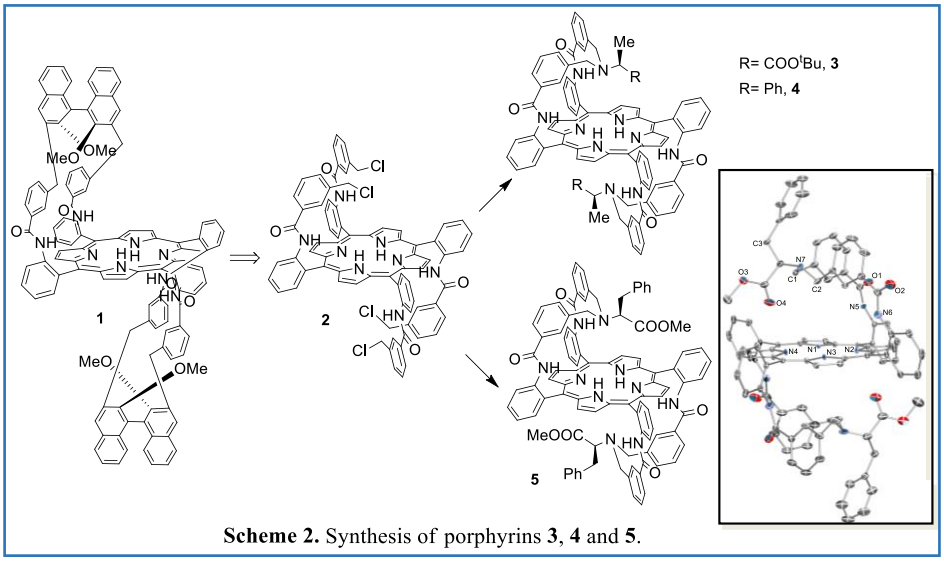
Scheme 1. General scheme of cyclopropanations.

Amongst all the applied catalysts, iron porphyrins, which show a cheap, eco-friendly and very active metal centre, have recently received a lot of attention also because they mimic the catalytic activity of enzymes containing an iron-heme unit.

We recently reported on the catalytic activity of C_2-symmetrical Fe^{III}(**1**)OMe complex which was efficient in promoting cyclopropanations with excellent diastereo- and enantioselectivities (3,4).

In order to increase the bio-compatibility of iron porphyrin-catalysed cyclopropanations, the binaphthyl chiral unit of **1** was replaced by an amino ester functionality. The three new C_2-symmetrical iron porphyrin amino ester conjugates **2-5** were synthesised and fully characterised including the X-ray crystallographic analysis of **5** (Scheme 2) (5).

Fe^{III}(porphyrin)(OMe) complexes were tested in the reaction of α-methylstyrene with different diazo compounds, which afforded corresponding cyclopropanes with an excellent diastereoselectivity (*trans/cis* ratio up to 93:7) but with modest enantioselectivity. The DFT study, which was carried out to rationalise the lack of the reaction enantiocontrol, indicated that chiral amino acid residues were not effective to select an enantiomeric pathway because they were too far from the catalytic active metal centre.



Scheme 2. Synthesis of porphyrins **3**, **4** and **5**.

References:

1. W. A. Donaldson, *Tetrahedron*, 2001, **57**, 8589-8627.
2. D. Y. K. Chen, R. H. Pouwer and J.-A. Richard, *Chem. Soc. Rev.*, 2012, **41**, 4631-4642.
3. D. Intrieri, S. Le Gac, A. Caselli, E. Rose, B. Boitrel and E. Gallo, *Chem. Commun.*, 2014, **50**, 1811-1813.
4. D. M. Carminati, D. Intrieri, A. Caselli, S. Le Gac, B. Boitrel, L. Toma, L. Legani and E. Gallo, *Chem. Eur. J.*, 2016, **22**, 13599-13612.
5. D. M. Carminati, D. Intrieri, S. Le Gac, T. Roisnel, B. Boitrel, L. Toma, L. Legnani and E. Gallo, *New J. Chem.*, 2017, submitted. (2003) 15.juk.

Selective oxidation of alkenes by H_2O_2 catalysed by well-defined [Iron(III)(Pyridine-Containing Ligand)] complexes

Alessandro Caselli and Giorgio Tseberlidis

Department of Chemistry, Università degli Studi di Milano and ISTM-CNR-Milano, Via Golgi 19, 20133 Milan, Italy. E-mail: alessandro.caselli@unimi.it

The introduction of a pyridine moiety into the skeleton of a polyazamacrocyclic ligand affects both thermodynamic properties and coordination kinetics of the resulting metal complexes (1). These features have engendered a great interest of the scientific community in recent years. The applications of pyridine-containing macrocyclic ligands ranges from biology to supramolecular chemistry, encompassing MRI, molecular recognitions, materials and catalysis. Much of the efforts in the use of macrocyclic pyridine containing ligands have been devoted to the study of catalytic oxidation reactions. We report here the synthesis and characterization of [Fe(III)Pc-L's)] complexes (Pc-L = Pyiridine-Containing Ligand) and their catalytic applications in alkene epoxidation or *cis*-dihydroxylation reactions using H_2O_2 as the terminal oxidant under mild conditions (Figure). Depending on the anion employed for the synthesis of the iron(III) metal complex, we observed a completely reversed selectivity. When X = OTf, a selective *cis*-dihydroxylation reaction was observed. On the other hand, employing X = Cl, we obtained the epoxide as the major product (traces of aldehyde were observed at very high conversions). It should be pointed out that under otherwise identical reaction conditions, using $FeCl_3 \cdot 6H_2O$ as catalyst in the absence of the ligand, no reaction was observed.

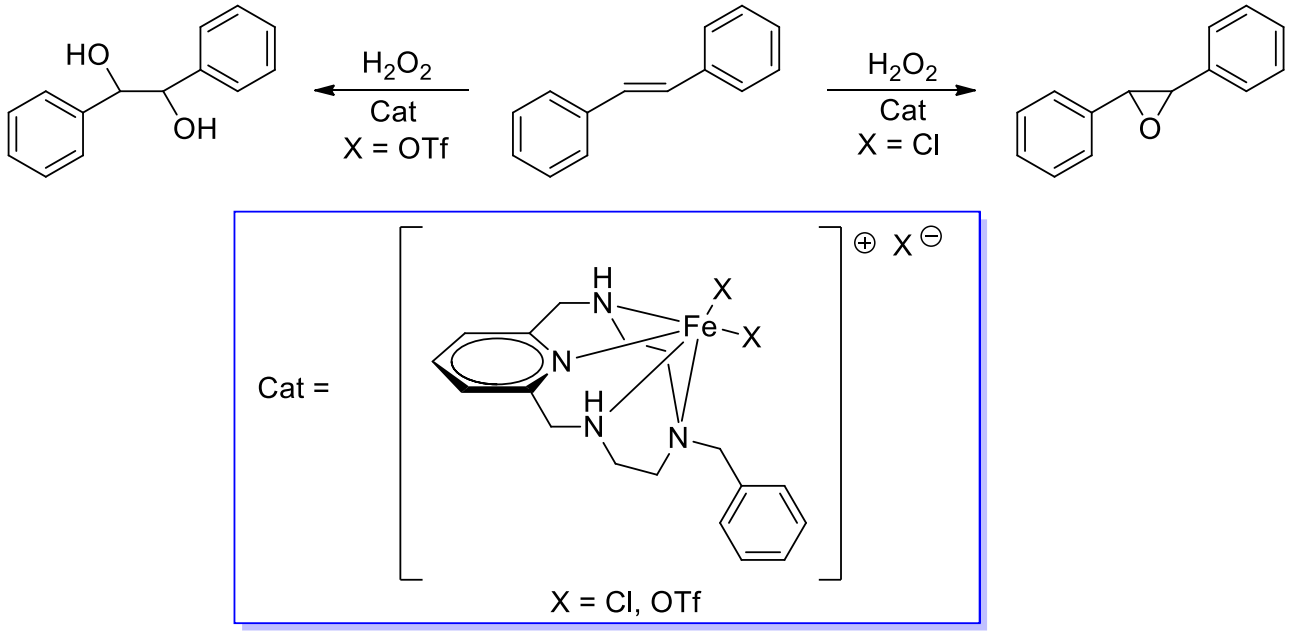


Figure Selective epoxidation or *cis*-dihydroxylation of alkenes catalysed by well-defined [Iron(III)(Pyridine-Containing Ligand)] complexes.

Key words: macrocyclic ligands, homogeneous catalysis, iron, oxidation reactions.

References:
[1] a) B. Castano, S. Guidone, E. Gallo, F. Ragaini, N. Casati, P. Macchi, M. Sisti, A. Caselli, *Dalton Trans.* **2013**, *42*, 2451; b) G. Tseberlidis, M. Dell'Acqua, D. Valcarenghi, E. Gallo, E. Rossi, G. Abbiati, A. Caselli, *RSC Adv.* **2016**, *6*, 97404; c) T. Pedrazzini, P. Pirovano, M. Dell'Acqua, F. Ragaini, P. Illiano, P. Macchi, G. Abbiati, A. Caselli, *Eur. J. Inorg. Chem.* **2015**, *2015*, 5089.

New quinoline-based chiral ligands and their Eu(III) complexes

Chiara De Rosa[a], *Marco Bettinelli*[a], *Fabio Piccinelli*[a]

[a] *Luminescent Materials Laboratory, DB, Università di Verona, and INSTM, UdR Verona, Strada Le Grazie 15, 37134 Verona, Italy;*
E-mail: chiara.derosa@univr.it

Luminescent complexes of Eu(III) and Tb(III) soluble in alcohol and water have been extensively exploited in biomedical field, as their excited states (in particular the ones of Tb(III) ion) are less sensitive to non-radiative vibrational quenching caused by high energy oscillators (such as OH) (1). This behaviour gives rise to reasonable values of the luminescence quantum yield. In addition, when a lanthanide complex is designed for biomedical applications, a strong overall luminosity or Brightness (B) is required, $B = \varepsilon \cdot \phi$, where ε is the molar absorption coefficient and ϕ the luminescence quantum yield. B can be increased if the ligand is capable to strongly absorb the exciting light and efficiently transfer the excitation energy to the lanthanide ion (*antenna effect*). In the presence of a chiral Ln(III) environment, the metal may also display circularly polarized luminescence (CPL), a chiroptical phenomenon, which has found interesting applications such as chirality sensing (2,3) and medical imaging techniques (4).
In this contribution we focus our attention on the synthesis and the characterization of new chiral ligands containing the quinoline fragment (Figure 1) and their Eu(III) complexes. We also discuss in detail, the luminescence spectroscopy of this complexes in the solid state and in solution of alchol and water.

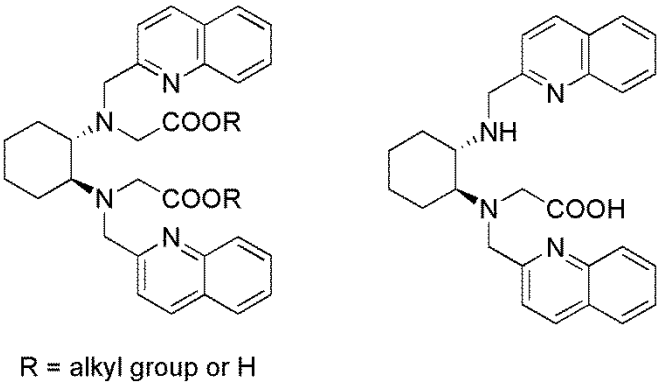


Figure 1. Molecular structure of the ligand discussed in the present contribution

References: 1. B. Di Bartolo and V. Goldberg, Radiationless Processes, Plenum Press, New York, 1980. 2. Yang, R. C. da Costa, M. J. Fuchter, A. J. Campbell, Nat. Photonics 7 (2013) 634 3. W. Sparks, J. Hough, L. Kolokolova, T. Germer, F. Chen, S. DasSarma , P. DasSarma, F. Robb, N. Manset, I. Reid, *J.* Quant. Spectrosc. Radiat. Transfer 110 (2009) 1771. 4. T. Novikova , A. Pierangelo, A. De Martino, A. Benali, P. Validire, Opt. Photonics News (2012) 26.

Stacking motives and solid state interactions of methylene blue cation in three unreported chloromercurate salts

Claudia Graiff, Stefano Canossa, Giovanni Predieri

Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, I-43124 Parma, Italy; claudia.graiff@unipr.it

Methylene blue (MB) is a renowned organic cation whose properties find application in a remarkably high number of science branches. The molecule, mostly used as chloride salt, whose formula structure is reported in Fig. 1 (left), features three condensed aromatic rings and two terminal dimethylamine groups, and its +1 charge is delocalized on the whole structure, with the only exception of the terminal methyl groups. This peculiar electronic panorama has important consequences on the physical and chemical properties of the molecule.

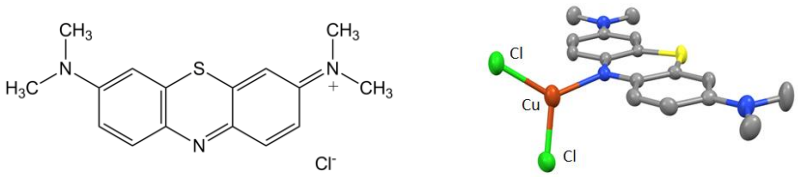


Figure 1. (Left) Formula structure of MBCl. (Right) Ortep view of (MB)$CuCl_2$ compound.

Aside from the many applications of MB in solutions, its properties in the solid state are less investigated. We recently reported (1) the first evidence of its coordinative capability by describing two crystalline phases in which MB is coordinated, together with two Cl atoms, by a Cu and an Ag metal centers respectively, resulting in two (MB)MCl_2 complexes (M= Cu, Ag). (See Fig. 1 (right)). This capability is due to the presence, on the middle aromatic N atom, of a localized partial negative charge which confers to the nitrogen lone pair a crucial Lewis basicity. Remarkably, we showed how this behavior is observed only in the solid state, sustained by supramolecular packing effects. Along with this recently discovered feature, actually, MB showed interesting supramolecular behaviors, since its arrangement in solid phases can vary depending on the other surrounding species.
Here we report studies on the behavior of MB towards mercury chlorometallates, undertaken to gain information regarding the MB-anion interactions, the overall packing features and how these influence the properties of the observed crystals. Three different compounds involving MB and $[HgCl_3]^-$, $[HgCl_4]^{2-}$ and $[HgCl_3]_n^{n-}$ chains respectively as anionic counterparts, have been synthesized by solid state reactions and structurally characterized by single crystal X-Ray diffraction. Remarkably, in the crystal packing of the three compounds, MB shows completely different stacking arrangements depending on the geometrical features and hindrance of the inorganic moiety. In the first case the π-stacking of the MB molecules is organized in a head-to-tail fashion. This is likely to be the most stabilizing geometrical configuration between different MB, because it allows the best match between the most positively and negatively charged part of the molecule (the S and the middle N atoms respectively).In the second case, the π-stacking is limited to MB dimers, arranged in a head to tail fashion as in the previous case. Dimers are packed together in a zig-zag fashion, and different MB pillars form square-shaped channels where the anions are accommodated. In the third case, MB arranges in head-to-head stacking, since the S atoms are oriented in the same direction. MB forms infinite pillars, each pillar being separated from the others by $[HgCl_3]_n^{n-}$ polymeric chains and nitromethane molecules.

References:
1. Stefano. Canossa, Alessia Bacchi, Claudia Graiff, Paolo Pelagatti, Giovanni Predieri, Andrea Ienco, Gabriele Manca, Carlo Mealli *Inorg. Chem*. **2017**, *56*, 3512−3516.

Chemical and electrochemical water oxidation catalyzed by iridium complexes

Gabriel Menendez Rodriguez[a,b], *Bas Van Dijk*[b], *Dennis Hetterscheid*[b], *Alceo Macchioni*[a]

[a] *Department of Chemistry, Biology and Biotechnology, University of Perugia and CIRCC, Via Elce di sotto, 8, 06123 Perugia, Italy;* [b] *Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands; gabriel.mr1988@gmail.com*

Water oxidation to molecular oxygen is a key half reaction in natural photosynthesis because it provides protons and electrons that can be exploited for the reduction of carbon dioxide to carbohydrates. Inspired by this natural process, people are intensely interested in water splitting using sunlight to convert and store solar energy into chemical energy (1). However, the efficiency of an artificial photosynthetic apparatus seems to be limited by the still unsatisfactory performance of the water oxidation catalytic pool. In our efforts to develop efficient water oxidation catalysts (WOCs), we recently reported hydroxy-pyridine-carboxylate iridium complexes (Figure 1) that exhibit remarkable activity in WO, when CAN (2) and $NaIO_4$ (3) were used as sacrificial oxidants.

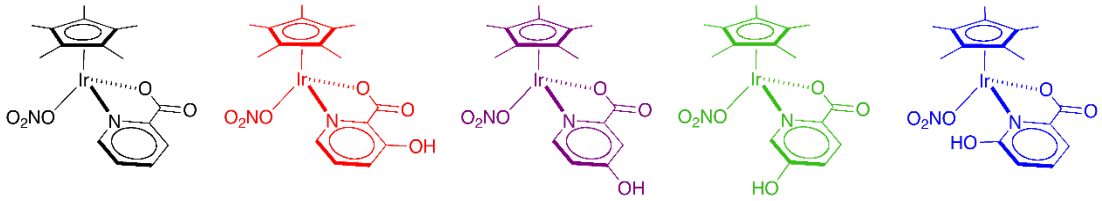


Figure 10. Water oxidation catalysts

Particularly, OH-containing complexes showed a similar TOF (23−28 min^{-1}), which was more than two times greater than that of pic (complex without OH), with CAN. Whereas the catalytic activity strongly depended on the position of the OH-substituent in the pyridine ring and pH with $NaIO_4$. The highest catalytic activity was observed for pic, which, at pH 7, showed a record TOF of 458 min^{-1} (3). More recently we found that complexes reported in Figure 1 are also active in electrocatalytic water oxidation. Also in this case, their performances were affected by the "oxidant" nature. When an ITO working electrode was used, catalytic activity was dramatically influenced by the position of the OH group substituent; on the contrary similar performances were obtained with a gold electrode.

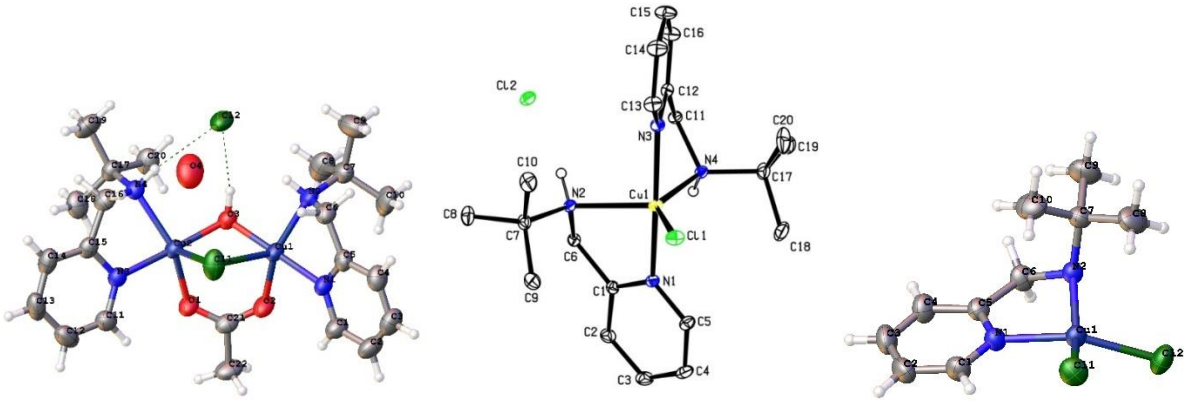
1. Armaroli, N. and Balzani, V., Chem. Eur. J. 22 (2016), 32.
2. Bucci, A., Savini, A., Rocchigiani, L., Zuccaccia, C., Rizzato, S., Albinati, A.; Llobet, A., Macchioni, A., Organometallics 31 (2012) 8071−8074.
3. Menendez Rodriguez, G., Bucci, A., Hutchinson, R., Bellachioma, G., Zuccaccia, C., Giovagnoli, S., Idriss, H. and Macchioni, A., ACS Energy Lett. 2 (2017) 105.

Syntheses, Structural characterization and chromotropism study of mono and dinuclear copper(II) complexes containing chelating ligand of 2-methyl-N-(pyridine-2-yl-methyl) propane-2-amine

Roya Nazari[a] *and Hamid Golchoubian*[a]

[a]*Department of Inorganic Chemistry, University of Mazandaran, Postal code 47416-95447, Babolsar, Iran; Roya.Nazari7@gmail.com*

Chromotropism is defined as a reversible color change of the materials caused by the surrounding chemical or physical stimulus; the stimuli could be solvent (solvatochromism), temperature (thermochromism), pressure (piezochromism), light (photochromism), pH (halochromism), ion (ionochromism) or electrons (electrochromism). Chromotropism has attracted much attention because of the wide variety of potential applications as thermosensitive materials, imaging, photo-switching materials, sensor materials, molecular switches, pollutant sensors and Lewis-acid-base color indicators. A combination of metal-ion recognition moieties with appropriate ligands has been reported to afford metal-ion responsive chromotropic molecules. Among chromotropic metal complexes, copper (II) ion with a combination of chelate ligands have been recognized as the most promising candidates for practical applications due to their high thermodynamic stabilities, accessibility of other oxidation states and also existence of simple and regular changes in their electronic spectra according to the strength of the stress imposed to the system (1,2,3). Here, a series of mono and dinuclear copper(II) complexes with chelating ligand of 2-methyl-N-(pyridine-2-yl-methyl)propane-2-amine, in which demonstrated distinctive solvato- and theromo- iono and halochromism properties is presented. The mechanism of the chromotropism in these compounds is discussed in detail.



References

1. H. Golchoubian, E. Rezaee, G. Bruno, H.A. Rudbari, Inorg. Chim. Acta, 366 (2011) 290-297.
2. H. Golchoubian, E. Rezaee, J. Mol. Struc., 927 (2009) 91-95.
3. W. Linert. Y. Fukuda, A. Camard, Coord. Chem. Rev., 218 (2001) 113-152.

Dependence of the second order NLO response of 5,15 *meso* push-pull Zn^{II} diarylporphyrins on complex aggregation phenomena

Francesca Tessore[a], *Gabriele Di Carlo*[a], *Alessio Orbelli Biroli*[b,c], *Maddalena Pizzotti*[a], *Stefania Righetto*[a], *Alessandra Forni*[b], *Alceo Macchioni*[d], *Luca Rocchigiani*[e]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Unità di Ricerca dell'INSTM, via C. Golgi 19-20133 Milano (Italy);* [b] *Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM, via C. Golgi 19-20133 Milano (Italy);* [c] *SmartMatLab Centre, via C. Golgi 19-20133 Milano (Italy);* [d] *Dipartimento di Chimica, Biologia e Biotecnologie and CIRCC, Università degli Studi di Perugia, via Elce di Sotto 8- 06123 Perugia (Italy);* [e] *School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ (United Kingdom)*

Email: francesca.tessore@unimi.it

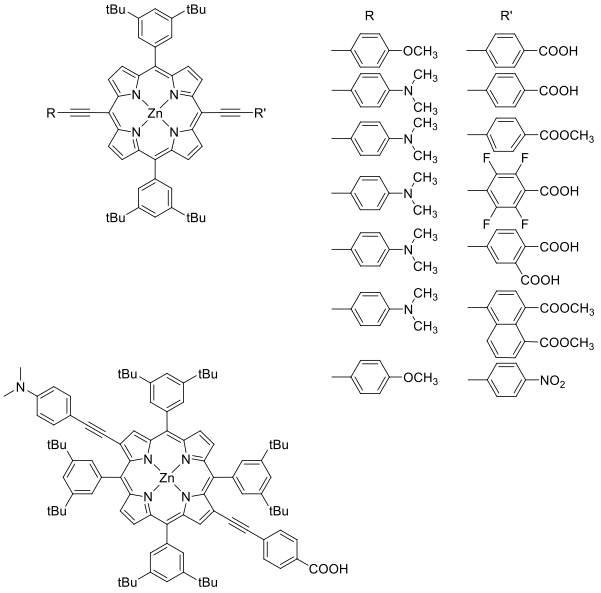


Figure 1

A series of 5,15 *meso* push-pull Zn^{II} diarylporphyrins, carrying one or two –COOH or –$COOCH_3$ acceptor groups and a –OCH_3 or a –$N(CH_3)_2$ donor group (Figure 1) show in both DMF and $CHCl_3$ solution a negative and solvent dependent second order NLO response measured by the EFISH technique (1), different from the structurally related Zn^{II} porphyrins carrying a –$N(CH_3)_2$ donor and a –NO_2 acceptor group, for which a still solvent dependent, but positive EFISH second order response was previously reported (2). Moreover, when a –$N(CH_3)_2$ donor group and a –COOH acceptor group are part of a sterically hindered 2,12 push-pull β-pyrrolic substituted Zn^{II} tetraaryl porphyrin, the EFISH response is positive and solvent independent. In order to rationalize these rather intriguing series of observations, EFISH measurements have been integrated by electronic absorption and infrared spectroscopic investigations and by DFT and CP-DFT theoretical and ^1H PGSE NMR investigations, which prompt that the significant concentration effects and the strong influence of the solvent nature on the NLO response are originated by a complex variety of aggregation processes induced by the –COOH group (Figure 2).

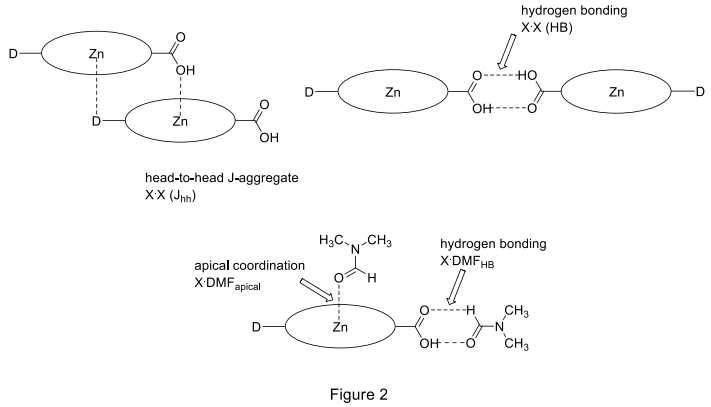


Figure 2

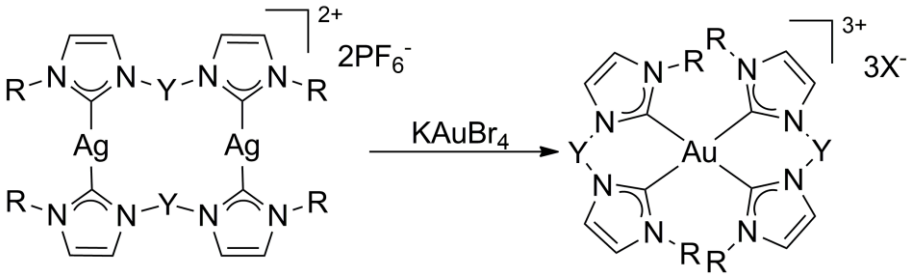
References: 1. Orbelli Biroli, A.; Tessore, F.; Righetto, S.; Forni, A.; Macchioni, A.; Rocchigiani, L.; Pizzotti, M.; Di Carlo, G. *Inorg. Chem.* **2017**, DOI: 10.1021/acs.inorgchem.7b00510. 2. Pizzotti, M.; Tessore, F.; Orbelli Biroli, A.; Ugo, R.; De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Zuccaccia, D.; Macchioni, A. *J. Phys. Chem. C* **2009**, *113*, 11131-11141.

Gold(III) bis-di(N-heterocyclic carbene) square planar trications as receptors towards halogen anions

Cristina Tubaro[a], *Marco Baron*[a], *Laura Orian*[a], *Valerio Di Marco*[a], *Marino Basato*[a], *Claudia Graiff*[b]

[a] *Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy;*
[b] *Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università degli Studi di Parma, Parco Area delle scienze 17/A, 43124 Parma, Italy.*
cristina.tubaro@unipd.it

NHC gold complexes are attractive for several applications, like for example catalysis, medicinal chemistry or material science. In this regard, while the examples of di(NHC) ligands coordinated to gold(I) centers are frequent, the number of gold(III) complexes remains still limited. We report here on the synthesis of mononuclear tricationic bis-di(NHC) gold(III) complexes, isolated by transmetalation of the ligand from the corresponding silver(I) complex to $KAuBr_4$. The counteranion of the gold(III) cationic complex depends on the adopted synthetic procedure. In the solid state, these complexes present interactions between the gold center and the halides of the counteranions, so that the geometry around gold is distorted pseudo-octahedral. Most interesting this interaction is maintained also in solution, thus suggesting the application of these compounds in anion sensing.(1,2) Titration studies with halides and DFT calculations clarified the formed species and the nature of the Au···X interaction.



References:
1. Gale, P.A., Howe, E.N.W. and Wu, X., Chem. 1 (2016) 351.
2. Langton, M.L., Serpell, C.J. and Beer, P.D., Angew. Chem. Int. Ed. 55 (2016) 1974.

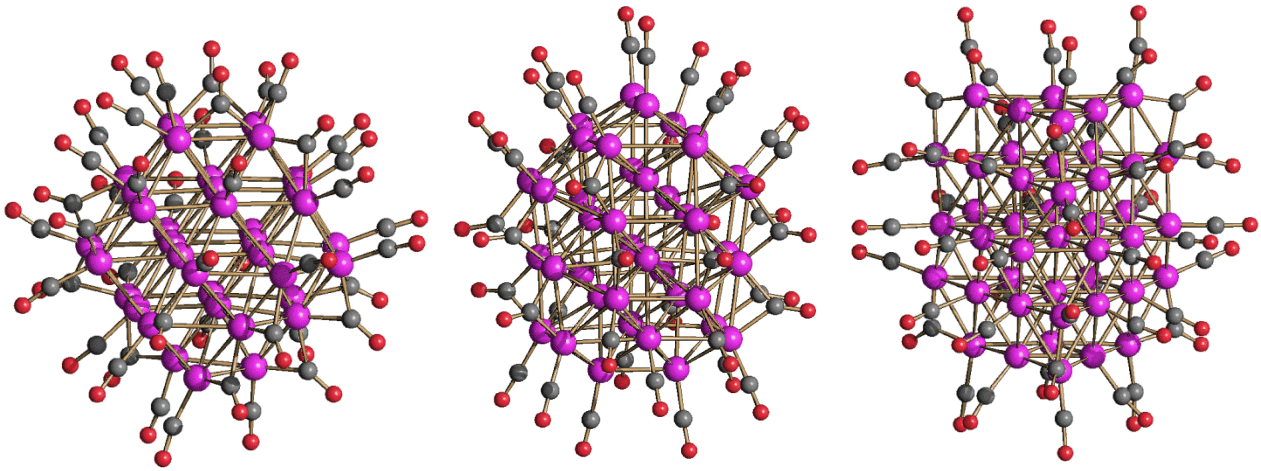
Globular molecular platinum carbonyl nanoclusters

Stefano Zacchini[a], *Iacopo Ciabatti*[a], *Cristina Femoni*[a], *Maria Carmela Iapalucci*[a], *Tiziana Funaioli*[b]

[a] *Dipartimento di Chimica Industriale "Toso Montanari" viale Risorgimento, 4 40136, Bologna"*; [b] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13 56124, Pisa; E-mail stefano.zacchini@unibo.it*

Homoleptic Pt-CO clusters can be grouped into two main categories depending of their CO content: (a) CO-rich clusters, the so called Chini clusters; (b) CO-poorer species, which can be referred as globular molecular platinum carbonyl nanoclusters or "platinum browns" (1). Globular platinum carbonyl clusters with almost regular structures may be viewed as molecular models of ultra-small metal nanoparticles (2). When defects are introduced, these respond with localized deformations which tend to eliminate and repair such defects (3). In addition, high-nuclearity platinum carbonyl clusters exhibit a rich redox chemistry: they undergo several reversible one-electron oxidation and reduction processes affording relatively stable species. In this respect, they may be viewed as molecular nanocapacitors and electron sinks (4).

Two general strategies are known for the preparation of globular Pt carbonyl nanoclusters: (a) thermal decomposition of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2-8) Chini clusters; (b) oxidation/reduction of preformed platinum browns (5). Herein, we report the synthesis and structural characterization of globular molecular platinum nanoclusters with nuclearities ranging from 14 up to 44 Pt atoms. Their metal cores may adopt *pp* (pentagonal prismatic), *bcc*, *ccp*, *hcp* or twinned *hcp/ccp* structures. Indeed, at these sub-nanometric length-scales there is not a clear structure/size relationship, being the overall structure the result of the balance of M-M and M-ligand interactions (6).



$[Pt_{36}(CO)_{44}]^{2-}$ $[Pt_{40}(CO)_{40}]^{4-}$ $[Pt_{44}(CO)_{45}]^{n-}$

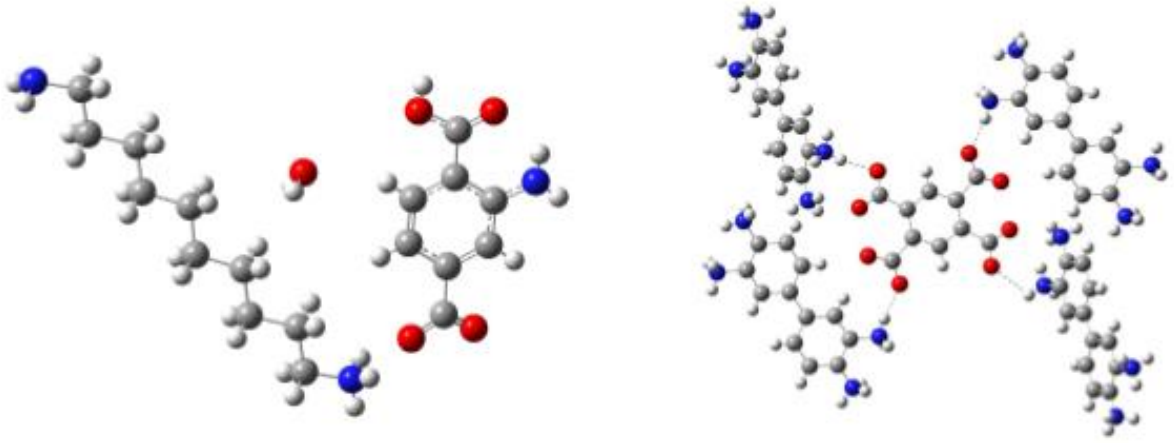
References: 1. I. Ciabatti, C. Femoni, M. C. Iapalucci, G. Longoni, S. Zacchini, *J. Clust. Sci.* **2014**, *25*, 115. 2. Y. Akdogan, S. Anantharaman, X. Liu, G. K. Lahiri, H. Bertagnolli, E. Roduner, *J. Phys. Chem. C* **2009**, *113*, 2352. 3. T. Imaoka, H. Kitazawa, W. -J. Chun, K. Yamamoto, *Angew. Che. Int. Ed.* **2015**, *54*, 9810. 4. C. Femoni, M. C. Iapalucci, F. Kaswalder, G. Longoni, S. Zacchini, *Coord. Chem. Rev.* **2006**, *250*, 1580. 5. E. Cattabriga, I. Ciabatti, C. Femoni, T. Funaioli, M. C. Iapalucci, S. Zacchini, *Inorg. Chem.* **2016**, *55*, 6068. 6. S. Zacchini, *Eur. J. Inorg. Chem.* **2011**, 4125.

Salts and cocrystals assembled from noncovalent associations between carboxylic acids and bases containing aromatic and aliphatic polyamine

Roya Nazari[a], Rim Ben debabis[b] ,G. Bruno[c] ,A. Saccà[c] and F. Nicolò[c]

[a]Department of Inorganic Chemistry, University of Mazandaran, Postal code 47416-95447, Babolsar, Iran; Roya.Nazari7@gmail.com .[b]Laboratory of Materials and Environmental Sciences, University of Sfax, BP 1171, 3000, Sfax, Tunisia. rim.bedbabis@yahoo.fr. [c]Department of Chemical, Biological, Pharmaceutical, and Environmental Sciences Viale Ferdinando. Stagno D'Alcontres, 31 98166 Messina, Italy

Multicomponent crystals and organic acid-base complexes have received considerable attention over the past few years (1). The design and construction of multicomponent supramolecular arrays utilizing noncovalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully employs hydrogen-bonding, halogen-bonding and the other types of noncovalent interactions, in building supramolecular systems (2,3). In the course of a wide-ranging study concerning the solid state aggregation of polyarboxylic acids and polyamines at different solvothemal conditions and under pH control, we obtained several supramolecular complex with total partial or without proton transfer depending on ΔpKa values. We will present a series of supramolecular structures and some associate ab-initio calculations.



1. a- M.J. Zaworotko, Cryst. Growth Des. 7 (2007) 4. (b) J.M. Lehn, Chem. Soc. Rev. 36 (2007) 151.

2. a- B. Kuhn, P. Mohr, M. Stahl, J. Med. Chem. 53 (2010) 2601.

3. a-J. E. Del Bene, I. Alkorta, and J. Elguero, J. Phys. Chem. A 2010, 114, 12958. b- Sakurai, M. Sundaralingam and G. A. Jeffrey, Acta Crystallogr., 16, 354 (1963). c- C.B. Aakeröy, J. Desper, B.A. Helfrich, P. Metrangolo, T. Pilati, G. Resnati and A. Stevenazzi, Chem. Commun. 2007, 4236 c

Antitumor activity of [Pt(*O,O'*-acac)(γ-acac)(DMS)] in MG-63 human osteosarcoma cells

Giovanna Antonaci [a], Luca Giulio Cossa [a], Antonella Muscella [b], Carla Vetrugno [b], Sandra Angelica De Pascali [c], Francesco Paolo Fanizzi [c], Santo Marsigliante [a]

[a]Laboratory of Cell Physiology, [b]Laboratory of Cell Phatology, [c]Laboratory of Inorganic Chemistry, Di.S.Te.B.A., University of Salento, via Provinciale Lecce Monteroni, 73100 Lecce, Italy

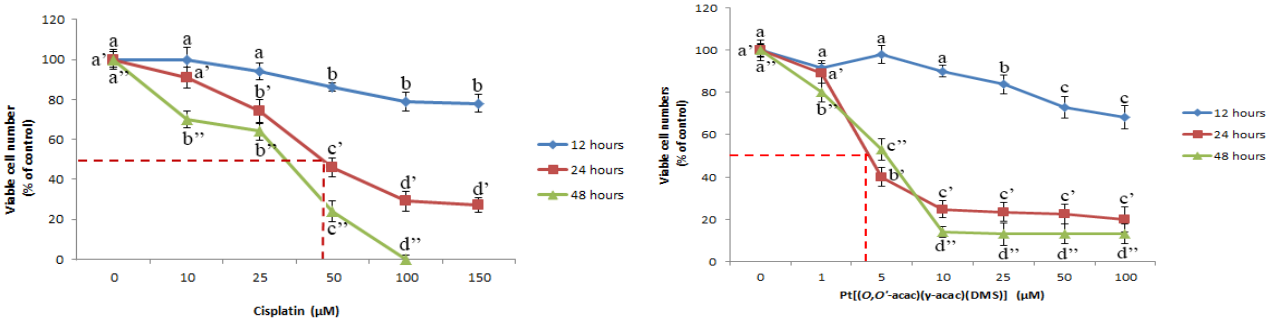
santo,marsigliante@unisalento.it,antonella.muscella@unisalento.it, fp.fanizzi@unisalento.it

Osteosarcoma (OS) is the most common malignant mesenchymal neoplasm amongst adolescents. Today, the regimen of methotrexate, adriamycin, and cisplatin (MAP) has become standard in North America and Europe. Despite this, an important number of patients will still develop fatal metastatic disease or serious complications of treatment, emphasizing the need for further clinical advancements.

In the present study, we investigated the potential citotoxicity of [Pt(*O,O'*-acac)(γ-acac)(DMS)] (Ptac2S), a Pt(II) drug having non genomic targets, on the MG-63 human osteosarcoma cell line. Ptac2S been tested in various cancer cells in opposition to cisplatin and results affirm that it induces fast and strong apoptosis death of cancer cells (1-3).

MG-63 cell were treated with various concentrations of Ptac2S and cisplatin and then cytotoxicities were assessed by using an 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenol tetrazolium bromide (MTT) assay. The citotoxicity of Ptac2S is approximately twelvefold greater than that observed for cisplatin (with IC_{50} of 4,5 ± 0,8 µM and 46,1 ± 3,2 µM for Ptac2S and cisplatin, respectively). Subsequent experiments, aimed at understanding the mechanisms of cell death triggered by Ptac2S, were made using a single concentration of Ptac2S (5 µM) and cisplatin (50 µM). It was found that Ptac2S provoked the activation of caspase-9 and -7 after 6 h treatment, whilst cisplatin provoked the activation of caspase 3 and -7 after 24 h treatment.

In conclusion, this study show that also in OS cells Ptac2S is far more citotoxic than cisplatin and that meanwhile both compounds provoked apoptosis, the activated caspases are different and the Ptac2S-provoked process is much more rapid.



References

1. Muscella A, Calabriso N, Fanizzi FP, De Pascali SA, Urso L, Ciccarese A, Migoni D, Marsigliante S. [Pt(O,O'-acac)(gamma-acac)(DMS)], a new Pt compound exerting fast cytotoxicity in MCF-7 breast cancer cells via the mitochondrial apoptotic pathway. Br J Pharmacol. 2008 Jan;153(1):34-49. Erratum in: Br J Pharmacol. 2008 Jan;153(1):175.

2. Muscella A, Calabriso N, Vetrugno C, Fanizzi FP, De Pascali SA, Marsigliante S. The signalling axis mediating neuronal apoptosis in response to [Pt(O,O'-acac)(γ-acac)(DMS)]. Biochem Pharmacol. 2011 Jun 1;81(11):1271-85.

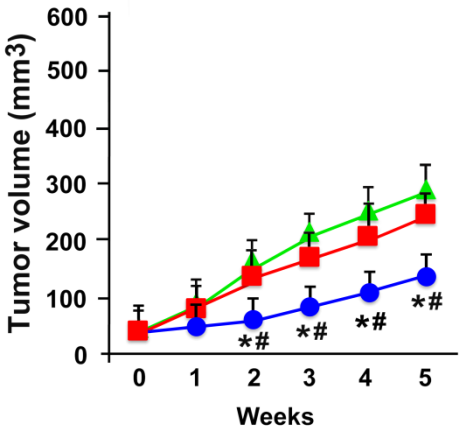
3. Muscella A, Calabriso N, De Pascali SA, Urso L, Ciccarese A, Fanizzi FP, Migoni D, Marsigliante S. New platinum(II) complexes containing both an O,O'-chelated acetylacetonate ligand and a sulfur ligand in the platinum coordination sphere induce apoptosis in HeLa cervical carcinoma cells. Biochem Pharmacol. 2007 Jun 30;74

Apoptosis by [Pt(*O,O'*-acac)(γ-acac)(DMS)] requires p53 activation in Malignant Pleural Mesothelioma

Antonella Muscella [a], Carla Vetrugno [a], Luca Giulio Cossa [b], Giovanna Antonaci [b], Sandra Angelica De Pascali [c], Francesco Paolo Fanizzi [c], Santo Marsigliante [b]

[a]*Laboratory of Cell Pathology,* [b]*Laboratory of Cell Physiology,* [c]*Laboratory of Inorganic Chemistry, Di.S.Te.B.A., University of Salento, via Provinciale Lecce Monteroni, 73100 Lecce, Italy*
antonella.muscella@unisalento.it, santo,marsigliante@unisalento.it, fp.fanizzi@unisalento.it,

Mesothelium cancer cells have epithelioid or sarcomatoid morphology. The worst prognosis is associated with sarcomatoid phenotype and resistance to therapy is affected by cells heterogeneity. We recently showed that in ZL55 mesothelioma cell line of epitheliod origin [Pt(*O,O'*-acac)(γ-acac)(DMS)] (Ptac2S) has an antiproliferative effect *in vitro* and *in vivo*. Aim of this work was to extend the study on the effects of Ptac2S on ZL34 cell line, representative of sarcomatoid mesothelioma. ZL34 cells were used to assay *in vivo* the antitumor activity of Ptac2S in a mouse xenograft model and, *in vitro*, the involvement of p53 protein in (a) the processes underlying the sensitivity to chemotherapy and (b) the activation of various transduction proteins involved in apoptosis/survival processes. Ptac2S increases ZL34 cell death *in vivo* compared with cisplatin and, *in vitro*, Ptac2S was more efficacious than cisplatin in inducing apoptosis (Figure). In Ptac2S-treated ZL34 cells, p53 regulated gene products of apoptotic BAX and anti-apoptotic Bcl-2 proteins via transcriptional activation (1).



	Average tumor size (mm^3)	% of control
Saline	285.11 ± 38.69	100
Cisplatin 10 mg/Kg	251.87 ± 49.36	88
Ptac2S 10 mg/Kg	133.72 ± 41.22	47

Results confirm that Ptac2S is a promising therapeutic agent for malignant mesothelioma (2), giving a substantial starting point for its further validation.

References

1. Muscella A., Vetrugno C, Cossa L. G., Antonaci G., Barca A., De Pascali S. A., Fanizzi F. P., Marsigliante S. Apoptosis by [Pt(O,O′-acac)(γ-acac)(DMS)] requires PKC-δ mediated p53 activation in malignant pleural mesothelioma. PlosOne July 2017 doi.org/10.1371/journal.pone.0181114

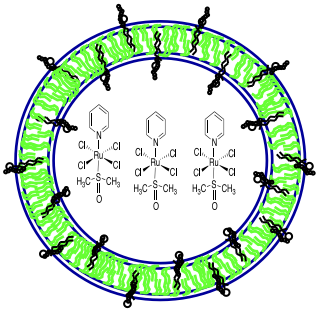
2.Muscella A., Vetrugno C., Cossa L. G., Antonaci G., De Nuccio F., De Pascali S. A.a, Fanizzi F. P., Marsigliante S. In Vitro and In Vivo Antitumor Activity of [Pt(O,O′-acac)(γ-acac)(DMS)] in Malignant Pleural Mesothelioma, . PlosOne november 2016 doi.org/10.1371/journal.pone.0165154

Ruthenium(III) complexes entrapped in liposomes with enhanced cytotoxic and anti-metastatic properties

D.Tesauro[a], M. E. Cucciolito,[b] R. Iannitti,[c] R. Palumbo,[c] G. Morelli,[a] F. Ruffo,[b,] A. D'Amora[b]

[a]Department of Pharmacy & CIRPeB, University of Naples Federico II, Via Mezzocannone, I-80134 Napoli; [b]Department of Chemical Sciences, University of Naples Federico II, Via Cintia, I-80126, Napoli; [c]Istituto di Biostrutture e Bioimmagini (IBB) CNR, Via Mezzocannone 16, 80134 Napoli,E-mail tesauro@unina.it

Metal-based anticancer drugs are pivotal in the fight against cancer pathologies. Since 1978 *cis*-platin was licensed for medical treatment of a wide number of tumor pathologies (1). However its chemiotherapic use is strongly limited by many and severe side effects and acquired tumor resistance. Since these limitations could be overcome by other metal complexes, in the last thirty years ruthenium compounds have been tested showing a remarkable antitumoral and antimetastatic activity associated with a lower toxicity. A hexacoordinate Ru(III) complex (NAMI-A) is currently undergoing advanced clinical evaluation (2). All data indicate that NAMI-A acts as a pro-drug, but the integrity of ruthenium complexes is essential to store the cytotoxic activity. In this scenario the condition of administration of ruthenium drugs are crucial to exploit their anticancer activity (3). In the last years innovative strategies have been produced to vehicle ruthenium ions in tumor cells like aggregates. This study aims to incorporate the ruthenium complexes in the inner aqueous compartment of liposomes and to test biological properties of two NAMI-A like pyridine derivatives. Specifically, we have investigated the pyridine derivatives of the sodium-compensated analogue of NAMI-A, Na[*trans*-$RuCl_4$(pyridine)(DMSO)] (NAMI-Pyr) and Na[*trans*-$RuCl_4$(Pytri)(DMSO)] (NAMI-Pytri). In thelatter complex the pyridine ligand is functionalized with a sugar moiety so as to increase biocompatibility and the ability to cross the cell membrane. The stability of the complexes was studied and compared in solution at different pH following UV-VIS spectra. Lipid formulations based on Egg PC were prepared adding Cholesterol, DSPE-PEG_{2000} joining molar ratio 57/38 /5% w/w respectively in MeOH/$CHCl_3$ (50/50 v/v) mixture and hydrated with 0.9% w/w of NaCl.



This composition was selected to reproduce analog supramolecular aggregates in clinical use to vehicle doxorubicin (Doxil). Ruthenium complexes were loaded into liposomes using the passive equilibration loading method. Full drug containing liposomes were structurally characterized by dynamic light scattering (DLS) measurements. Data indicate the formation of stable aggregates with size and shape in the right range for *in vivo* applications. The amount of encapsulated ruthenium complexes was quantified by means of ICP-AES. Stability and drug release properties of ruthenium containing liposomes were confirmed in buffer. The growth inhibitory effects of both liposomal and free complexes drug were tested on prostate cancer cells (PC3). Preliminary results show high cytotoxic effect of ruthenium complexes delivered by supramolecular aggregates with respect to free complexes drug.

References:
1. L. Kelland *Nat. Rev. Cancer* 2007, **7**:573–84.
2. E.Alessio *Eur.J. Inorg. Chem* 2017, 1549–1560,
3. B.M. Blunden, M.H. Stenzel *J.Chem.Technol.Biotechnol.* 2015, 90: 1177‑1195.

Elenco degli Autori

*Indica Autore presentatore

Nicoletti Vincenzo Giuseppe	INO OR15
Nicolini Valentina	INO OR47
Nicolo Francesco	INO PO35
Novakovic Rada	INO PO18
Oberhauser Werner	ORG/INO PZ02
Orbelli Biroli Alessio	INO PO32
	INO OR32
Orian Laura	INO PO33
Orteca Giulia	INO PO10
Osella Domenico	INO PO08
	INO OR22
Pagliaro Miaria V.	INO PO19
	ORG/INO PZ02
Palermo Giovanna	INO OR49
Palumbo Rosanna	INO PO38
Pampaloni Guido	INO PO01
Pandini Giuseppe	INO OR15
Panunzi Barbara	INO OR29
	INO OR11
Paolo Carloni*	INO PL02
Paolucci Francesco	INO OR33
Paradiso Veronica	INO OR39
Paradiso Veronica*	INO PO23
Pardo Emilio	INO KN07
Patzke Greta	INO OR28
Pavone Michele	TEO/INO OR01
Pavone Vincenzo	INO PO04
	INO PO11
	INO OR02
	INO OR21
	INO OR23
Pedroni Marco	INO OR45
Pellecchia Claudio	INO PO15
	INO OR27
Pellei Maura	INO OR09
Pelosi Giorgio	INO PO03
	INO PO09
Perfetti Mauro*	INO OR31
Perin Elena*	INO PO08
Peruzzini Maurizio	INO OR26
	INO OR06
Pettinari Claudio	INO PO20
Piazzetta Paolo	TEO/INO OR04
Piccinellia Fabio	INO PO28
Piccirillo Susanna	INO PO05
	INO PO24
Pield Markus	INO PO10
Pietraperzia Giangaetano	INO OR10
Pietropaolo Adriana	INO OR15
Pietrosanti Chiara	INO OR09
Piotto Srefano	INO OR11
	INO OR29
Pirovano Valentina*	ORG/INO PZ01

Pirro Fabio	INO PO04
Pizzotti Maddalena	INO PO32
	INO OR32
Poggini Lorenzo	INO OR31
Porchia Marina	INO OR09
Pragliola Stefania*	INO OR44
Pratesi Alessandro	INO OR14
Prati laura*	INO OR03
Prato Maurizio	INO OR33
Predieri Giovanni	INO PO29
Prejanò Mario	TEO/INO OR04
Priola Emanuele	INO OR43
Proto Antonio	INO OR24
Puzzo Francesco	ORG/INO OR04
Ragazzon Giulio*	INO PZ01
Rancan Marzio	INO OR42
Ravera Mauro	INO PO08
	INO OR22
Re Nazzareno	INO PO05
Reale Andrea	INO OR08
Regina Claudia	TEO/INO OR06
Restivo Francesco Maria	INO PO03
Reverchon Ernesto	INO OR13
Ricciardi Loredana	INO OR49
Righetto Stefania	INO PO32
	INO OR32
Rizzarelli Enrico	INO OR15
Roberta Sessoli	INO OR38
Robertino Zanoni*	INO KN03
Roberto Fattorusso	INO KN05
Rocchigiani Luca	INO PO32
	INO OR32
Rogolino Dominga	INO PO03
Rogolino Dominga*	INO PO09
Roisnel Thierry	INO PO26
Romeo Andrea Romeo	INO PO22
Rosato Antonio	INO OR18
Rösch Frank	INO PO10
Rossi Elisabetta	ORG/INO PZ01
Rossin Andrea	INO OR41
Rotili Dante	INO PO13
Rovai Donella	INO OR31
Roveri Norberto	INO PO07
Rubagotti Sara	INO PO10
Rubino Alfredo	INO OR44
Ruggieri Silvia	INO OR37
Ruffo Francesco	INO PO38
Russo Nino	TEO/INO OR04
	TEO/INO OR06
Sacca Alessandro	INO PO35
Saccone Adriana	INO OR04
Sainctavit Philippe	INO OR31
Saladini Monica*	INO PO10
Samaritani Simona	INO OR40

Samaritani Simona*	INO OR12
Sancey Lucie	INO OR49
Santi Marta	INO PO02
Santini Carlo	INO OR09
Satriano Cristina	INO OR15
Saturnino Carmela	INO OR17
Scaramuzzo Francesca	INO PO13
Scibetta Emanuele	INO PO24
Scolaro Luigi Monsù	INO PO22
Secchi Valeria	INO PO02
Serri Michele	INO OR31
Sessa Lucia	INO OR11
Sessoli Roberta	INO OR31
Sibilia Concita	INO OR36
Silvi Serena	INO PO16
	INO OR07
	INO PZ01
Sinicropi Maria Stefania	INO OR17
Solokha Pavlo*	INO OR04
Sonia Di Gaetano	INO KN05
Sorace Lorenzo	INO OR38
Soriente Annunziata	INO OR13
Speghini Adolfo*	INO OR45
Szerb Elisabeta I.	INO OR49
Tagliabue Andrea	ORG/INO OR04
Tavantia Francesco	INO PO10
Tegoni Matteo	INO PO09
Termine Roberto	INO OR49
Tesauro Diego*	INO PO38
Tesi Lorenzo	INO OR38
Tessore Francesca*	INO PO32
Tessore Francesca*	INO OR32
Testa Giovanna	INO PO13
Tisato Francesco	INO OR09
Toma Lucio	INO PO26
Trapani Mariachiara*	INO PO22
Travaglia Alessio	INO OR15
Tseberlidis Giorgio	INO PO27
Tubaro Cristina	INO OR42
Tubaro Cristina*	INO PO33

	INO KN08
Tuci Giulia	INO OR41
Ugliengo Piero	TEO/INO OR02
Valeri Sergio	INO OR47
Valtancoli Barbara	INO OR10
Van Dijk Bas	INO PO30
Velardo Amalia	INO OR44
Venditti Iole	INO PO02
	INO PO13
	INO OR36
Venditti Iole*	INO OR09
Venditto Vincenzo	INO OR44
Vetrugno Carla	INO PO36
	INO PO37
Vigliotta Giovanni	INO OR13
Vilar Ramon	INO OR22
Villa alberto	INO OR03
Villari Enrica	INO OR08
Viola Elisa	INO OR19
Vizza Francesco	INO PO19
	INO OR33
	ORG/INO PZ02
Volpi Giorgio	INO OR30
Vummaleti Sai V. C.	INO PO17
Weber Michael D.	INO OR30
Zacchini Stefano	INO PO01
	INO OR37
Zacchini Stefano*	INO PO34
Zambrano Gerardo	INO OR21
Zambrano Gerardo*	INO PO11
Zanellato Ilaria	INO PO08
Zani Claudia	INO PO03
Zanoni Robertino	INO OR35
Zanotti Valerio	INO PO01
	ORG/INO OR04
Zanotti-Gerosa Antonio	ORG/INO OR03
	ORG/INO OR05
Zongo L.	INO OR46
Zouari Fatma	INO PO25

DIVISIONE DI CHIMICA DEI SISTEMI BIOLOGICI

Comitato Scientifico

- Carla Isernia, Università degli Studi della Campania “Luigi Vanvitelli”
- Roberto Purrello, Università degli Studi di Catania
- Massimiliano Coletta, Università degli Studi di Roma Tor Vergata
- Antonio Rosato, Università degli Studi di Firenze
- Michael Assfalg, Università degli Studi di Verona
- Stefano Ciurli, Università degli Studi di Bologna
- Luca D’Andrea, Consiglio Nazionale delle Ricerche
- Alessandro D’Urso, Università degli Studi di Catania
- Gianluca Fossati, Italfarmaco SpA
- Luca Prodi, Università degli Studi di Bologna

Delegato di Divisione

- Luigi Russo, Università degli Studi della Campania “Luigi Vanvitelli”

Programma Scientifico

Divisione di Chimica dei Sistemi Biologici

Lunedì 11 Settembre 2017

	Sala Diana
Sessione della Divisione di Chimica dei Sistemi Biologici	
Chairpersons R. Purrello, S. Ciurli	
9.00 – 9.50	CSB PL01: M. J. Maroney, J.O. Campeciño, C.E. Carr, H.Q. Hu, H.T. Huang, Musiani F. and S. Ciurli *Bioinorganic chemistry from metals to enzymes: A nickel tour.*
9.50 – 10.10	CSB OR01: L. Mazzei, F. Musiani, G. Lente, M. Palombo, M. Cianci, S. Benini and S. Ciurli. *Biochemical and structural studies on the inhibition of urease, a nickel-dependent virulence factor.*
10.10 – 10.30	CSB OR02: C. Pozzi, S. Ciambellotti, C. Bernacchioni, F. Di Pisa, P. Turano and S. Mangani. *Structural and mechanistic insights into iron processing and biomineralization by vertebrate ferritins*
10.30 – 11.00	Coffee Break
Sessione congiunta con la Divisione di Chimica Fisica dedicata al Prof. Guido Barone	
Chairpersons C. Isernia, C. Giancola	
11.00 – 11.50	CSB PL02: M.R. Tiné. *Calorimetry and Thermoanalytical Techniques in the Study of Proteins.*
11.50 – 12.05	Divisione di Chimica Fisica: R. Oliva. *Biophysical studies of membrane perturbation induced by the antimicrobial peptide GKY20*
12.05 – 12.20	CSB OR03: A. D'Urso, C.M.A. Gangemi, S. Alaimo, A. Pulvirenti, A. Ferro and R. Purrello. *Exploiting conformation and structural analysis of endogenous miRNAs to refine gene targeting evaluation.*
12.20 – 12.35	Divisione di Chimica Fisica: A. Del Giudice. *The structural response of Human Serum Albumin to oxidation: a biological buffer to local formation of hypochlorite.*
12.35 – 12.50	CSB OR04: J. Amato. *Identification and characterization of DNA G-quadruplex interacting proteins.*

13.00 - 14.00	Intervallo Pranzo

	Sala Diana
Sessione della Divisione di Chimica dei Sistemi Biologici	
Chairpersons M.J. Maroney, A. Rosato	
15.00 – 15.50	CSB PL03: R. Fattorusso. *Protein folding pathways investigated by NMR spectroscopy.*
15.50 – 16.10	CSB OR05: D. Marasco, E. Novellino and S. La Manna. *Insights in self-recognition, misfolding and mislocalization mechanisms of Nucleophosmin 1 in Acute Myeloid Leukemia.*
16.10 – 16.30	CSB OR06: L. Russo, K. Giller, E. Pfitzner, C. Griesinger and Stefan Becker. *The molecular recognition mechanism of the coactivator NCoA-1 by STAT6.*
16.30 – 17.00	Coffee Break
Sessione della Divisione di Chimica dei Sistemi Biologici	
Chairpersons G. Fossati, A. D'Urso	

17.00 – 17.30	Premio Divisione di Chimica dei Sistemi Biologici- Italfarmaco CSB PL04: S. Sattin *Towards unconventional therapeutic approaches.*
17.30 – 17.45	CSB OR07: M. Prejanò, T. Marino, and N. Russo. *How can work methanol dehydrogenase from Methylacidiphilum fumariolicum with the alien Ce(III) ion in the active center? A theoretical study.*
17.45 – 18.00	CSB OR08: V. Maggi, F. Bianchini, A. Sartori and R. Fiammengo. *Aminoproline-RGD functionalized gold nanoparticles for targeting of integrins involved in tumor angiogenesis.*
18.00– 18.15	CSB OR09: V. Oliveri, S. Zimbone, M. L. Giuffrida, F. M. Tomasello, F. Bellia, G. Vecchio. *Functionalized cyclodextrins as modulators of Aβ cytotoxicity.*
18.15– 18.30	CSB OR10: A. Bortot, F. Munari, S. Zanzoni, M. D'Onofrio, D. Fushman and M. Assfalg. *Specific secondary interactions between ubiquitin and UBA observed in cell-mimicking crowded solution.*
18.30– 18.45	CSB OR11: M. Gaeta, R. Randazzo, D. A. Cristaldi, A. D'Urso, R. Purrello and M. E. Fragalà. *ZnTPPS demetallation: role of polyelectrolytes on aggregation after protonation in acid.*
18.45– 19.00	CSB OR12: F. Arcudi and M. Prato. *Synthesis, Separation and Characterization of Small and Highly Fluorescent Nitrogen-Doped Carbon NanoDots.*
	Sala Diana
19.00– 20.00	*Assemblea dei Soci della Divisione di Chimica dei Sistemi Biologici*

Martedì 12 Settembre 2017

	Sala Diana
Sessione congiunta con il gruppo Interdivisionale di Biotecnologie	
Chairpersons L. Cipolla, M. Coletta	
9.00 – 9.50	CSB PL05: D. Montesarchio. *Multifunctional nanosystems for theranostics.*
9.50 – 10.10	CSB OR13: M. Gobbo, F. Biscaglia, S. Rajendran, C. Benna, G. Bocchinfuso, P. Conflitti, L. Litti, R. Sommaggio, D. Nitti, A. Rosato, A. Palleschi, S. Mocellin and M. Meneghetti. *Peptide Targeted Gold Nanostructures for high effective SERRS Imaging of Colorectal Cancer Cells.*
10.10 – 10.30	Divisione di Chimica Organica: G. Oliviero, M. Marzano, A.P. Falanga, S. D'Errico, G. Piccialli, N. Borbone. *Higher order G-quadruplex-based aptamers from tetra-end-linked oligonucleotides with in vitro anti-HIV activity*
10.30 – 11.00	Coffee Break
Sessione della Divisione di Chimica dei Sistemi Biologici	
Chairpersons M. Assfalg, R. Fattorusso	
11.00 – 11.50	CSB PL06: S. C. Baffoni. *Unravelling the molecular mechanisms of iron-sulfur protein maturation.*
11.50 – 12.05	CSB OR14: D. Sala, S. Ciambellotti, A. Giachetti, P. Turano and A. Rosato. *Investigation of the iron(II) release mechanism from human ferritin as a function of pH.*
12.05 – 12.20	CSB OR15: D. Capasso, S. Di Gaetano, V. Celentano, D. Diana, L. Festa, R. Di Stasi, L. De Rosa, R. Fattorusso and L. D. D'Andrea. *Unveiling a VEGF-mimetic peptide sequence in IQGAP1 protein.*
12.20 – 12.35	CSB OR16: M. Scognamiglio and B. Schneider. *Metabolomics studies of allelopathy: unravelling chemical interactions between Mediterranean plants through an omics approach.*

12.35 – 12.50	CSB OR17: A. P. Falanga, N. Borbone, S. D'Errico, B. Pinto, M. Marzano, G. Piccialli and G. Oliviero. *Targeting of the G-quadruplex-forming bcl2G4-1 region in the human Bcl-2 gene with Peptide Nucleic Acid: an anti-gene approach for cancer treatment.*
12.50 – 13.05	CSB OR18: M. De Zotti, A. Bortolotto, I. Elmaghraby, L. Sella, F. Favaron. *Peptaibols: naturally occurring peptides as biopesticides.*

13.05 - 14.00	Intervallo Pranzo

	Sala Paestum B
14:00-15:00	*Sessione Poster 2 (CSB PO01 – CSB PO20)*

Premi
della Divisione di Chimica dei Sistemi Biologici

Premio Italfarmaco

Sara Sattin, Università degli Studi di Milano

Towards unconventional therapeutic approaches

Sara Sattin

Università degli Studi di Milano, Dipartimento di Chimica, via Golgi, 19, 20133, Milano

Complex and often multifactorial diseases, such as cancer and cystic fibrosis, but also apparently simpler microbial infections, represent an increasing burden for our society and it is becoming clear that they are increasingly difficult to control with traditional therapeutic approaches. Thus, in many areas of medicine, unconventional approaches are currently being sought out to overcome this problem.

One example of unconventional thinking consists of the idea that modulation, rather than straightforward inhibition, of hub proteins, such as the chaperone Hsp90, may represent a promising approach to achieve selective control of complex signalling pathways.(1) In a collaboration with the Colombo group, fine-tuning of Hsp90 dynamics, resulting in activation of its ATPase activity, was achieved with a family of benzofuran derivatives designed to act as allosteric modulators of the chaperone. These molecules have shown promising downstream effects.(2,3,4)

In a second example, inhibition of the first step of microbial infections,(5) *i.e.* pathogen adhesion to the host, was studied as a complementary approach to classical anti-infective agents. Anti-adhesion therapy allows clearance of the infective agent while exerting minimal selective pressure, a very important feature in order to avoid the insurgence of antimicrobial resistance. DC-SIGN is a human dendritic cells receptor that act as an adhesion factor by recognizing highly mannosylated glycoproteins present on several pathogens. Some of them (*e.g.* HIV-1, Ebola, measles, *C. albicans*, etc.) exploit this otherwise protective mechanism for host adhesion and invasion. Inhibition of DC-SIGN with aptly designed polyvalent ligands leads to effective inhibition of the infection process.(6)

References: 1. Sattin, S.; Tao, J.; Vettoretti, G.; Moroni, E.; Pennati, M.; Lopergolo, A.; Morelli, L.; Bugatti, A.; Zuehlke, A.; Moses, M.; Beebe, K.; Rusnati, M.; Neckers, L.; Zaffaroni, N.; Agard, D.A.; Bernardi, A. and Colombo, G. *Chem. Eur. J.*, 2015, *21*, 13598-13608. 2. Sattin, S.; Panza, M.; Vasile, F.; Berni, F.; Goti, G.; Tao, J.; Agard, D.; Colombo, G. and Bernardi, A.*Eur. J. Org. Chem.* 2016, *2016(20)*, 3349-3364. 3. Vettoretti, G.; Moroni, E; Sattin, S.; Tao, J.; Agard, D.A.; Bernardi, A. and Colombo, G. *Sci. Rep*. 2016, *6*, 23830. 4. Bagdany, M.; Veit, G.; Fukuda, R.; Avramescu, R.G.; Okiyoneda, T.; Baaklini, I.; Singh, J.; Sovak, G.; Xu, h.; Apaja, P.M.; Sattin, S.; Beitel, L.K.; Roldan, A.; Colombo, G.; Balch, W.; Young, J.C.; Lukacs, G. L. *Nat. Commun.* 2017, *accepted*. 5. Sattin, S. and Bernardi, A. *Trends Biotechnol.* 2016, 34(6), 483-495. 6. Mauro, N.; Ferruti, P.; Ranucci, E.; Manfredi, A.; Berzi, A.; Clerici, M.; Cagno, V.; Lembo, D.; Palmioli, A. and Sattin, S. *Sci. Rep.* 2016, *6*, 33393.

Conferenze Plenarie

- CSB PL01: Maroney M.J., University of Massachusetts
- CSB PL02: Tinè M. R., Università di Pisa
- CSB PL03: Fattorusso R., Università della Campania "Luigi Vanvitelli"
- CSB PL04: Sattin S., Università degli Studi di Milano
- CSB PL05: Montesarchio D., Università di Napoli "Federico II"
- CSB PL06: Ciofi Baffoni S., Università di Firenze

Bioinorganic chemistry from metals to enzymes: A nickel tour

Maroney M.J.[a,b], Campeciño J.O.[a], Carr C.E.[a], Hu H.Q.[b], Huang H.T.[a], Musiani F.[c] and Ciurli S.[c]

[a]University of Massachusetts, Department of Chemistry, Amherst, MA USA 0100;
[b]University of Massachusetts, Graduate Program in Molecular and Cellular Biology, Amherst, MA USA 01003;
[c]Laboratory of Bioinorganic Chemistry, Department of Pharmacy and Biotechnology, University of Bologna, Via Fanin 40, I-40127 Bologna, Italy

Since the discovery of nickel in jack bean urease ca. 1975, the biological roles for nickel have increased to encompass enzymes that catalyze at least eight different chemical reactions (1). Perhaps the most surprising of these are redox reactions associated with hydrogenase, CO-dehydrogenase, acetyl-coenzymeA synthase, and a nickel-dependent superoxide dismutase, NiSOD, all of which access the Ni(III) oxidation state—an oxidation state that is unstable for Ni ions in an aqueous environment. NiSOD offers the clearest view of Ni redox chemistry, since it contains no other metal ions. The Ni center employs two cysteinate ligands and three types of N-donor ligands—a histidine imidazole, a backbone amidate, and the N-terminal amine. Using a structure/function approach, the roles for these ligands in generating a redox-active Ni center will be discussed, and reveals a surprising role for the amine/amidate combination in stabilizing the desired redox chemistry (2). To supply Ni for enzymes, microorganisms have developed trafficking systems that generate specific biological responses to Ni-binding.

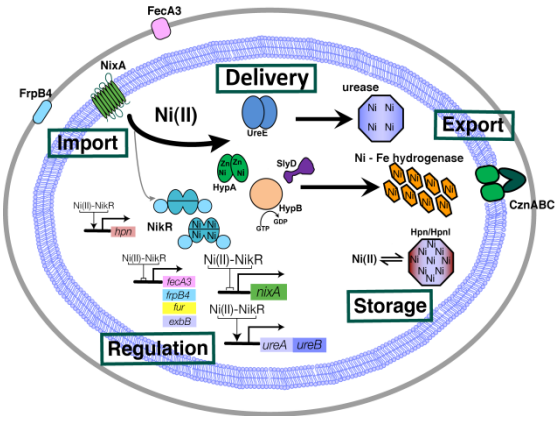


Figure 1. Overview of Ni Trafficking in *H. pylori*

These proteins include importers, exporters, transcriptional regulators, and metallochaperones, each of which must discriminate Ni(II) from the pool of available metals in the cell. The mechanisms of metal discrimination in Ni trafficking proteins will also be explored. The studies reveal the importance of the N-terminal amine in the complexes of RcnR (3), a transcriptional regulator in E. coli, and in H. pylori HypA (4), an unusual metallochaperone in this human pathogen.

References: 1. M. J. Maroney, S. Ciurli Chemical Reviews (2014), 114, 4206. 2. 2. J. O. Campeciño, M. J. Maroney, In The Biological Chemistry of Nickel; Zamble, D., Rowinska-Zyrek, M., Kozlowski, H., Eds.; The Royal Society of Chemistry: (2017) 10, 170. 3. K. A. Higgins, P. T. Chivers, M. J. Maroney, J. Am. Chem. Soc. (2012), 134, 7081. 4. H. Q. Hu, R. C. Johnson, D. S. Merrell, M. J. Maroney Biochemistry (2017,) 56, 1105.

Calorimetry and Thermoanalytical Techniques in the Study of Proteins

Maria Rosaria Tiné.

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi 13, 56124- Pisa

Thermal analysis and calorimetry, particularly when combined with other analytical and spectroscopic techniques, offer powerful methods for studying biological macromolecules. Here, we present and discuss the application of calorimetry and thermogravimetric analysis to the study of the conformational behavior of proteins in three cases belonging to very different fields, ranging from the use as binders in tempera paintings, to medical or pharmaceutical applications.

The first issue concerns with proteinaceous materials used as paint media in order to disperse and apply pigments. Over the centuries, animal glue, egg and milk or casein have been the most common proteinaceous binders used in tempera technique. The characterization of these paints is complex because of the sample size, the high inorganic content, the degradation phenomena undergone with time, and the simultaneous presence of other organic materials. We used a combined approach (Thermogravimetric Analysis, TGA, Differential Scanning Calorimetry, DSC, Fourier Transform Infrared Spectroscopy, FTIR) to investigate the interaction occurring between selected pigments and ovalbumin, casein, and rabbit glue as well as their changes with ageing. This allowed us to characterize the molecular modifications undergone by proteins as an effect of light ageing, and depending on the pigment, in terms of amino acid side chain oxidations, cross linking/aggregation, hydrolysis, and the formation of stable complexes. We highlighted that in most cases the inorganic pigments interact with proteins by decreasing their thermal stability and their intermolecular β-sheet content, and that ageing induces aggregation.

The second issue concerns with some biocompatible nanomaterials suitable to be used in biotechnological and medical applications. We focused our attention on alloysite nanotubes (HNTs) which are considered very promising as nanocarriers, because of their low cost, high availability, biocompatibility, atoxicity, anti-inflammatory properties, and capacity to maintain the biological activity of immobilized enzymes. HNTs can be loaded with a wide range of molecules, from antioxidants to antibiotics, anticancer, and anti-inflammatory drugs and can be used for drug delivery, as tablets and capsule fillers. Therefore, to study their interaction with proteins is important because of the general concern regarding the safety of nanoparticles and the modifications that loaded biological material may undergo with alteration of their biological functions. We studied the interaction between HNTs and some proteins (bovine serum albumin, α-lactalbumin and β–lactoglobulin) loaded into HTNs, by using TGA and FTIR. These techniques enable us to assess the protein conformation and thermal stability, respectively, and to estimate the amount of protein loaded into the HNTs.

Finally, as the third issue, we show here some preliminary results on the use of protein-polymer conjugates in order to improve the properties of therapeutic proteins. It is well known that proteins and peptides exhibit great potentialities as therapeutic agents; however, they also show severe drawbacks (low solubility in water, tendency to agglomerate during storage in solution, short shelf-life, rapid kidney clearance, destruction by proteolytic enzymes, propensity to generate neutralizing antibodies). One of the most promising modification for overcoming these drawbacks is the covalent attachment of synthetic polymers (the most common being PEG) to the protein, to form protein-polymer conjugates with the aim of improving both the stability and the pharmacokinetics properties of the drug. In particular, we present some preliminary results obtained by TGA and DSC measurements on Myoglobin-PEG and myoglobin-polyphosphoesters conjugates. In fact, polyphosphoesters (PPEs) are one of the most promising new classes of polymers in biomedicine.

Protein folding pathways investigated by NMR spectroscopy

Roberto Fattorusso.

Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Via Vivaldi 43, 81100, Caserta; roberto.fattorusso@unicampania.it

Protein folding represents one of the most intensively studied phenomena of recent times in biology, but nonetheless the molecular mechanisms by which a peptide chain reaches its native structure have not been yet fully understood (1,2). Importantly, understanding protein folding pathways plays an essential role in the comprehension of many diseases rooted in the protein misfolding processes, also considering that every functional protein is permanently in equilibrium with its unfolded state (3). As a matter of fact, evolutionary selection favoured protein structures characterized by folding pathways preventing the formation of uncontrolled protein misfolded states, which in some peculiar conditions, either pathological or physiological, may anyhow take place.
Here, the investigation, by means of NMR and other peculiar methodologies, of protein folding mechanisms, which may help in the comprehension of misfolding molecular processes, will be described.

References : 1. S. E. Jackson *Fold. Des.* 3, R81-91 (1998). 2. S. Amani and A. Naeem *Int. J. Biol. Macromol*. 58, 104-112 (2013). 3. M. Sadqi, M, D. Fushman, & Muñoz *Nature* 442, 317-21 (2006).

Towards unconventional therapeutic approaches

Sara Sattin

Università degli Studi di Milano, Dipartimento di Chimica, via Golgi, 19, 20133, Milano

Complex and often multifactorial diseases, such as cancer and cystic fibrosis, but also apparently simpler microbial infections, represent an increasing burden for our society and it is becoming clear that they are increasingly difficult to control with traditional therapeutic approaches. Thus, in many areas of medicine, unconventional approaches are currently being sought out to overcome this problem.

One example of unconventional thinking consists of the idea that modulation, rather than straightforward inhibition, of hub proteins, such as the chaperone Hsp90, may represent a promising approach to achieve selective control of complex signalling pathways.(1) In a collaboration with the Colombo group, fine-tuning of Hsp90 dynamics, resulting in activation of its ATPase activity, was achieved with a family of benzofuran derivatives designed to act as allosteric modulators of the chaperone. These molecules have shown promising downstream effects.(2,3,4)

In a second example, inhibition of the first step of microbial infections,(5) *i.e.* pathogen adhesion to the host, was studied as a complementary approach to classical anti-infective agents. Anti-adhesion therapy allows clearance of the infective agent while exerting minimal selective pressure, a very important feature in order to avoid the insurgence of antimicrobial resistance. DC-SIGN is a human dendritic cells receptor that act as an adhesion factor by recognizing highly mannosylated glycoproteins present on several pathogens. Some of them (*e.g.* HIV-1, Ebola, measles, *C. albicans*, etc.) exploit this otherwise protective mechanism for host adhesion and invasion. Inhibition of DC-SIGN with aptly designed polyvalent ligands leads to effective inhibition of the infection process.(6)

References: 1. Sattin, S.; Tao, J.; Vettoretti, G.; Moroni, E.; Pennati, M.; Lopergolo, A.; Morelli, L.; Bugatti, A.; Zuehlke, A.; Moses, M.; Beebe, K.; Rusnati, M.; Neckers, L.; Zaffaroni, N.; Agard, D.A.; Bernardi, A. and Colombo, G. *Chem. Eur. J.*, 2015, *21*, 13598-13608. 2. Sattin, S.; Panza, M.; Vasile, F.; Berni, F.; Goti, G.; Tao, J.; Agard, D.; Colombo, G. and Bernardi, A.*Eur. J. Org. Chem.* 2016, *2016(20)*, 3349-3364. 3. Vettoretti, G.; Moroni, E; Sattin, S.; Tao, J.; Agard, D.A.; Bernardi, A. and Colombo, G. *Sci. Rep*. 2016, *6*, 23830. 4. Bagdany, M.; Veit, G.; Fukuda, R.; Avramescu, R.G.; Okiyoneda, T.; Baaklini, I.; Singh, J.; Sovak, G.; Xu, h.; Apaja, P.M.; Sattin, S.; Beitel, L.K.; Roldan, A.; Colombo, G.; Balch, W.; Young, J.C.; Lukacs, G. L. *Nat. Commun.* 2017, *accepted*. 5. Sattin, S. and Bernardi, A. *Trends Biotechnol*. 2016, 34(6), 483-495. 6. Mauro, N.; Ferruti, P.; Ranucci, E.; Manfredi, A.; Berzi, A.; Clerici, M.; Cagno, V.; Lembo, D.; Palmioli, A. and Sattin, S. *Sci. Rep.* 2016, *6*, 33393.

Multifunctional nanosystems for theranostics

Daniela Montesarchio.

Department of Chemical Sciences, University of Napoli Federico II, Via Cintia 21, 80126 Napoli, Italy; daniela.montesarchio@unina.it

The development of multifunctional systems for potential applications in theranostic nanomedicine, aimed at simultaneously providing the diagnosis and treatment of a disease, is one of the hottest fields in current biomedical research.[1] For the construction of these tools, different kinds of nanosystems can be selected, decorated with multiple functional units (ranging from small bioactive molecules to targeting ligands) using various anchoring methods, and investigated as optimal scaffolds for the *in vivo* delivery of drugs and imaging agents.[2] Following this general strategy, the nanoplatforms loaded with both therapeutic and diagnostic agents can be mere carriers, in some cases, or introduce further functional activities, in others.

In this frame, a small library of multifunctional nanoparticles, differing for the nature of the nanoparticle core/coating and of the active ingredient, will be here presented.

In light of the chosen approach, the active functional agents are *ad hoc* designed and synthesized with suitable tethers so to allow their efficient incorporation into the selected nanocarrier (*i.e.*, streptavidin-coated silica nanoparticles, superparamagnetic nanoparticles or liposomes), thus exploiting different recognition schemes (*i.e.*, selective recognition, hydrophobic or electrostatic interactions).

Data on the *in vitro* activity of these multifunctional nanoparticles as theranostic agents towards specific pathologies, such as cancer and clotting disorders, will be also discussed.

References: 1. T. Lammers *et al*., *Acc. Chem. Res*. 2011, *44*, 1029-1038. 2. For a recent review, see for example: E.-K. Lim *et al*., *Chem. Rev*. 2015, *115*, 327−394. 3. G. Mangiapia *et al*., *Biomaterials* 2012, *33*, 3770–3782. 4. G. Mangiapia *et al*., *Biomacromolecules* 2013, *14*, 2549-2560. 5. G. Vitiello *et al*., *J. Mater. Chem. B* 2015, *3*, 3011–3023. 6. A. Luchini *et al*., *Nanoscale* 2016, *8*, 10078-10086. 7. C. Riccardi *et al*., *Eur. J. Org. Chem.* 2017, 1100–1119. 8. C. Riccardi *et al*., manuscript under review.

Unravelling the molecular mechanisms of iron-sulfur protein maturation

Simone Ciofi Baffoni.

University of Florence, CERM and Department of Chemistry, Via L. Sacconi 6, Sesto Fiorentino, Italy; ciofi@cerm.unifi.it

Iron-sulfur (Fe-S) clusters have long been recognized as essential and versatile cofactors of proteins involved in catalysis, electron transport and sensing of ambient conditions. Despite the relative simplicity of Fe-S clusters in terms of structure and composition, their synthesis and assembly into apo proteins is a highly complex and coordinated process in living cells. Different biogenesis machineries in both bacteria and eukaryotes have been discovered that assist Fe-S protein maturation. Molecular mechanisms of Fe-S protein maturation will be presented showing how an integrated structural biology approach can fully describe the pathways responsible of Fe-S cluster synthesis and incorporation into apo proteins (1, 2, 3). The investigation of these mechanisms will undoubtedly enhance our ability to identify and treat known disorders of Fe-S cluster biogenesis and to recognize hitherto undescribed Fe-S cluster-related diseases.

References: 1. Banci L, Ciofi-Baffoni S, Gajda K, Muzzioli R, Peruzzini R, Winkelmann J. Nat Chem Biol. 2015, 11:772-8. 2. Banci L, Camponeschi F, Ciofi-Baffoni S, Muzzioli R. J Am Chem Soc. 2015, 137:16133-43. 3. Brancaccio D, Gallo A, Piccioli M, Novellino E, Ciofi-Baffoni S, Banci L. J Am Chem Soc. 2015, 137:16133-43.

Comunicazioni Orali

Biochemical and structural studies on the inhibition of urease, a nickel-dependent virulence factor

Luca Mazzei [a], Francesco Musiani [a], Gabor Lente [b], Marta Palombo [a], Michele Cianci [c], Stefano Benini[d] and Stefano Ciurli [a].

[a] Dept. of Pharmacy and Biotechnology, University of Bologna (Italy);
[b] Dept. of Inorganic and Analytical Chemistry, University of Debrecen (Hungary);
[c] Dept. of Agricultural, Food and Environmental Sciences, Università Politecnica delle Marche (Italy);
[d] Faculty of Science and Technology, Free University of Bolzano (Italy); luca.mazzei2@unibo.it

Urease is a Ni(II)-dependent enzyme that catalyzes the hydrolysis of urea to give ammonia and CO_2, determining an overall pH increase and causing negative effects for human health as well as agriculture (1). Hence, the scientific community has devoted intense efforts in the last decades for the development of efficient inhibitors of urease able to counteract its negative effects (1).

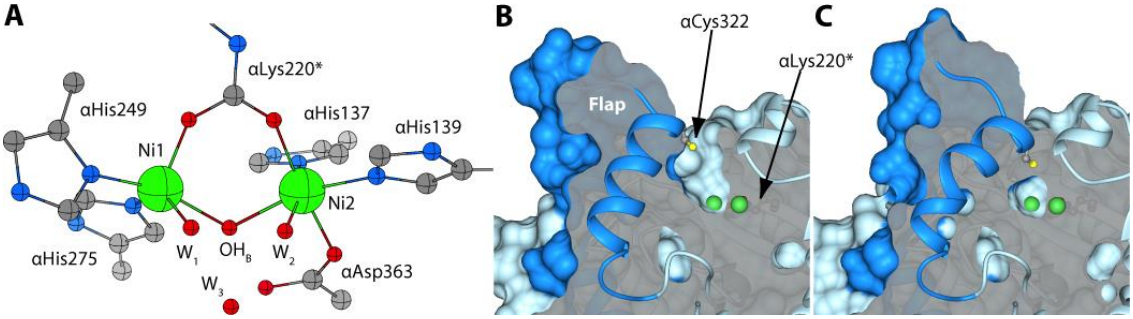


Figure 1. (A) Coordination environment of the Ni(II) ions in the active site of urease from *Sporosarcina pasteurii* (SPU). (B and C) Longitudinal section of the open (B) and closed (C) conformations of the flexible flap in SPU.

In this work, a combination of kinetic experiments and X-ray protein crystallography has been applied to the urease system in order to determine the inhibition mode of several known urease inhibitors: i) fluoride, ii) sulphite, iii) 1,4-benzoquinone (BQ), iv) catechol (CAT) and v) N-butylthiophosphotriamide (NBPT). Both fluoride and sulphite show a pH-dependent inhibition on urease, directly binding to the two Ni(II) ions in the enzyme active site (2,3). Unlike the previous cases, BQ and CAT act as time-dependent urease inhibitors covalently binding to a conserved cysteine residue located on a flexible flap that controls the access of the substrate to the active site cavity (4,5). NBPT, a commercial nitrogen stabilizer extensively used in agriculture, acts as a slow-binding inhibitor of urease. In particular, it directly interacts with the nickel ions in the urease active site, undergoing an *in situ* hydrolysis that generates a tetrahedral moiety blocking the active site and precluding the enzyme from further substrate hydrolysis (6).
All the results shown in this work will be useful to develop, through a structure-based drug design procedure, novel and more efficient urease inhibitors.

References: 1. L. Mazzei, F. Musiani, S. Ciurli - Urease, in "The Biological Chemistry of Nickel" (2017) pp. 60-97. 2. S. Benini, M. Cianci, L. Mazzei, S. Ciurli - *J. Biol. Inorg. Chem.* (2014) 19:1243. 3. L. Mazzei, M. Cianci, S. Benini, F. Musiani, L. Bertini, S. Ciurli - *J. Inorg. Biochem.* (2016) 154:42. 4. L. Mazzei, M. Cianci, F. Musiani, S. Ciurli - *Dalton Trans.* (2016) 45:5455. 5. L. Mazzei, M. Cianci, F. Musiani, G. Lente, M. Palombo, S. Ciurli - *J. Inorg. Biochem.* (2017), 166:182. 6. L. Mazzei, M. Cianci, F. Musiani, S. Ciurli - *in preparation.*

Structural and mechanistic insights into iron processing and biomineralization by vertebrate ferritins

Cecilia Pozzi[a], Silvia Ciambellotti[b,c], Caterina Bernacchioni[b,c], Flavio Di Pisa[a], Paola Turano[b,c] and Stefano Mangani[a,b].

[a] Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Siena, Italy; [b] CERM, University of Florence, Sesto Fiorentino (FI), Italy; [c] Department of Chemistry, University of Florence, Sesto Fiorentino (FI), Italy; pozzi4@unisi.it

Ferritins are ubiquitous multimeric protein systems showing a nanocage structure able to include thousands of iron atoms as oxoferric biomineral. In mammals, these twentyfour-mer protein shells are generally heteropolymers composed by two different types of subunits classified, according to their relative molecular weight, as heavy H and light L (183 and 175 amino acids, respectively, in human chains). The relative ratios between the two types in heteropolymers is tissue-dependent: ferritins in iron storage organs (e.g. liver and spleen) are richer in L-subunits, while those with fast iron metabolism (e.g. brain and heart) are richer in the H type. The H-subunit contains a ferroxidase center characterized by the so-called Fe1 and Fe2 sites and able to rapidly oxidize Fe^{2+} to Fe^{3+}. Besides the high structural conservation of the catalytic center, the mechanism by which the ferroxidase reaction occurs is not fully understood and different models have been proposed. We have developed a soaking/flash freezing method to allow aerobic and anaerobic addition of iron(II) to frog and human ferritin crystals (1,2,3) Multi-wavelength anomalous diffraction data have been exploited to unambiguously detect iron atoms. Through this method we have observed for the first time the iron binding sites in X-ray crystal structures of vertebrate ferritins and how they become populated with time (1,2,3). Interestingly, accessories transient metal sites have also been identified in the proximity of the ferroxidase site and demonstrated to play a key role in the reaction turnover (3,4). On the other hand, L-subunits lack the ferroxidase site, and hence iron incorporation in nanocages rich in L-chains is much slower. Nevertheless, homopolymeric L-ferritins are able to biomineralize iron. The proposed mechanism involves the presence of a putative nucleation site on the inner cage surface (5). Through a time-dependent series of X-ray crystal structures of iron-loaded homopolymeric human L-ferritin we have observed the progressive formation of a triiron cluster on the inner cage surface of each subunit (6). After 60 minutes exposure, a fully formed (μ^3-oxo)tris[(μ^2-peroxo)(μ^2-glutamato-κ*O*:κ*O*')](glutamato-κ*O*)(diaquo)triiron(III) anionic cluster was clearly visible in a structure determined at 1.98 Å resolution. The functional significance of the protein carboxylates involved in the coordination of the metallocluster for biomineralization was clearly demonstrated by the lower iron oxidation rate measured in the E60A-E61A-E64A triple variant of human L-ferritin. A similar metallocluster was also observed in the lower resolution (2.22 Å) structure of horse spleen ferritin, suggesting that it constitutes a common feature of mammalian ferritins representing the yet unobserved, nucleation site of L-type proteins. This cluster structure is unprecedent in biological systems even though it shows striking structural similarities to a synthetic hexanuclear iron cluster reported about 20 years ago and proposed as possible model of a ferritin biomineral (7). Structural data, together with stopped-flow kinetic data, provide new clues to explain the ferroxidase and biomineralization processes in vertebrate ferritins.

References: 1. I Bertini, D Lalli, S Mangani, C Pozzi, C Rosa, EC Theil, P Turano, *JACS* 2012, *134*, 6169-6176. 2. C Pozzi, F Di Pisa, C Bernacchioni, S Ciambellotti, P Turano, S Mangani, *Acta Crystallogr D Biol Crystallogr.* 2015, *71*, 1909-1920. 3. C Pozzi, F Di Pisa, D Lalli, C Rosa, EC Theil, P Turano, S Mangani, *Acta Crystallogr D Biol Crystallogr.* 2015, *71*, 941-953. 4. C Bernacchioni, C Pozzi, F Di Pisa, S Mangani, P Turano. *Chemistry*. 2016, *22*, 16213-16219. 5. T Granier, G Comberton, B Gallois, BL d'Estaintot, A Dautant, RR Crichton, G Précigoux, *Proteins.* 1998, *31*, 477-485. 6. C Pozzi, S Ciambellotti, C Bernacchioni, F Di Pisa, S Mangani, P Turano, *Proc Natl Acad Sci U S A.* 2017, *114*, 2580-2585. 7. I Shweky, LE Pence, GC Papaefthymiou, R Sessoli, W Yun, A Bino, SJ Lippard, *J. Am. Chem. Soc.* 1997, *119*, 1037-1042.

Exploiting conformation and structural analysis of endogenous miRNAs to refine gene targeting evaluation

Alessandro D'Urso[a], *Chiara Maria Antonietta Gangemi*[a], *Salvatore Alaimo*[b], *Alfredo Pulvirenti*[b], *Alfredo Ferro*[b] *and Roberto Purrello*[a].

[a] *Dipartimento di Scienze Chimiche, Università degli studi di Catania;* [b] *Department of Clinical and Experimental Medicine University of Catania Italy c/o Dipartimento di Matematica e Informatica;* adurso@unict.it

Mature microRNAs (miRNAs) are a class of evolutionally conserved, single-stranded, small (approximately 19−23 nucleotides), endogenously expressed, and non-protein-coding RNAs that act as post-transcriptional regulators of gene expression in a broad range of animals, plants, and viruses.(1,2) The biogenesis of miRNAs is a multiple step process, which complete with the incorporation of the mature miRNA into RNA-induced silencing complex.(3) The RISC complex functions by perfectly or imperfectly matching with its complementary target mRNA, and induces target mRNA degradation or translational inhibition. Thus, alterative expression of miRNAs has been associated with a number of diseases, genetic disorders and tumors progression.(3)
We think that the knowledge of the miRNA structure may give a new insight into miRNA-dependent gene regulation mechanism and be a step forward in the understanding their function and involvement in cancerogenesis. With this aim we characterized the conformation and structures adopted by several endogenous miRNA in physiological conditions. Preliminary data obtained by CD melting experiments, using synthetic miRNA,(4) highlighted the important role played by the structures adopted by miRNA. Indeed the sequences showed a sigmoidal CD melting curves induced a significant inhibition of the luciferase activity for two of the most prominent genes associated to lung cancer, c-MET and Epidermal Growth Factor Receptor (EGFR).

References: 1. Bartel, D. P. *Cell* **2004**, 116, 281. 2. He, L.; Hannon, G. J. *Nat. Rev. Genet.* **2004**, 5, 522. 3. Haifeng Dong, Jianping Lei, Lin Ding, Yongqiang Wen, Huangxian Ju, and Xueji Zhang. *Chem Rev* **2013,** *113*(8), 6207. 4. A. Laganà, M. Acunzo, G. Romano, A. Pulvirenti, D. Veneziano, L. Cascione, R. Giugno, P. Gasparini, D. Shasha, A. Ferro and C. M. Croce. *Nuc. Ac. Res.*

Identification and characterization of DNA G-quadruplex interacting proteins

Jussara Amato.

Department of Pharmacy, University of Naples Federico II, via D. Montesano 49, 80131 Napoli, Italy; jussara.amato@unina.it

Guanine-rich DNA sequences can form non-canonical structures known as G-quadruplexes (G4s). These peculiar structural arrangements emerged as biologically significant due to compelling evidence that they participate in several biological processes. Experimental evidences imply that G4 DNA structures are, for example, involved in tumorigenic processes, probably with regulatory functions, and that various proteins are involved in the recognition of these structures and modulate their effect on such processes.

The analysis of the G4–protein interaction network can be considered a crucial point to clarify the elusive biological mechanisms in which such relevant DNA structures could be implicated. Some proteins are able to recognize G4 structures and some are also able to unfold them. The discovery of these proteins raises interesting questions regarding the dynamic nature and function of such structures within the genome, especially at telomere, a region of repetitive G-rich sequences at each end of chromosomes. In this frame, we decided to search for proteins able to recognize G4-forming truncations of human telomeric DNA sequence (1). In particular, we employed a chemoproteomic-driven approach, where the molecule of interest is used as a bait to fish out its interactors from nuclear extracts. In particular, we have used different G4 conformations, namely the parallel and the anti-parallel folds. Very interestingly, novel G4-interacting partners were identified, thus suggesting a possible, and so far unknown, role of these proteins. In this communication, the latest results will be presented, including a preliminary structural study of the interaction between the HMGB1 protein and the parallel telomeric G4 structure.

References: 1. Pagano, B.; Margarucci, L.; Zizza, P.; Amato, J.; Iaccarino, N.; Cassiano, C.; Salvati, E.; Novellino, E.; Biroccio, A.; Casapullo, A.; Randazzo, A. *Chem. Commun.* **2015**, *51*, 2964–2967.

Insights in self-recognition, misfolding and mislocalization mechanisms of Nucleophosmin 1 in Acute Myeloid Leukemia

Daniela Marasco, Ettore Novellino and Sara La Manna.

Department of Pharmacy, University of Naples "Federico II", 80134, Naples; daniela.marasco@unina.it

In protein misfolding processes the amyloid fibrillization is a unique ordered state governed by specific patterns of molecular interactions (1). Normally folded proteins can access to amyloidogenic states that are often considered as an ensemble of native-like conformations with locally unfolded elements. The characterization of these amyloidogenic species is crucial to elucidate potential aggregation under native conditions and for *in vivo* aggregation events (2). Nucleophosmin (NPM1) is a multifunctional protein involved in a variety of biological processes and implicated in the pathogenesis of several human malignancies, it was also identified as the most frequently mutated gene in 30% of Acute Myeloid Leukemia (AML) patients. This protein is endowed with a modular structure: the C-terminal domain (CTD) has a three helix bundle tertiary structure: H1 (243-259), H2 (264-277) and H3 (280-294) helices constitute the CTD and fold through a compact transition state and unfolds keeping a residual secondary structure at the interface between H2 and H3 helices (3). To gain insights into the role of isolated fragments in NPM1's biological functions we dissected the CTD in its helical fragments: we showed that the intrinsically unfolded regions of NPM1 significantly contribute to the binding of c-MYC G-quadruplex motif and that H1 helix is endowed with an unusual thermal stability (4). Lately we demonstrated that the H2 (5,6) and H3 AML mutated regions (7) form amyloid-like assemblies endowed with fibrillar morphology and β-sheet structure that resulted toxic in cell viability assays. Actually, our mechanistic hypothesis is that the AML-associated mutations destabilize the α-helical structure of the H3 region in the native NPM1 and disrupts the CTD tertiary structure predisposing it to the formation of toxic aggregates since it induces the exposure of the H2 and H3 regions. These findings could have implications in AML molecular mechanisms caused by NPM1 mutants.

References: 1. F. Bemporad, A. De Simone, F. Chiti, C.M. Dobson, Biophysical journal, 102 (2012) 2595-2604.2. M. Landreh, A. Rising, J. Presto, H. Jornvall, J. Johansson, J Biol Chem, 290 (2015) 26430-26436.3. C.G. Grummitt, F.M. Townsley, C.M. Johnson, A.J. Warren, M. Bycroft, The Journal of biological chemistry, 283(2008) 23326-23332.4. P.L. Scognamiglio, C. Di Natale, M. Leone, M. Poletto, L. Vitagliano, G. Tell, D. Marasco, Biochimica et biophysica acta, 1840 (2014) 2050-2059. 5. C. Di Natale, P.L. Scognamiglio, R. Cascella, C. Cecchi, A. Russo, M. Leone, A. Penco, A. Relini, L. Federici, A. Di Matteo, F. Chiti, L. Vitagliano, D. Marasco, FASEB journal, (2015).6. A. Russo, C. Diaferia, S. La Manna, C. Giannini, T. Sibillano, A. Accardo, G. Morelli, E. Novellino, D. Marasco, Biochimica et biophysica acta, 1865 (2017) 176-185.7. P.L. Scognamiglio, C. Di Natale, M. Leone, R. Cascella, C. Cecchi, L. Lirussi, G. Antoniali, D. Riccardi, G. Morelli, G. Tell, F. Chiti, D. Marasco, Oncotarget, (2016) 7(37):59129-59143.

The molecular recognition mechanism of the coactivator NCoA-1 by STAT6

Luigi Russo[a,b], *Karin Giller*[b], *Edith Pfitzner*[c], *Christian Griesinger*[b] *and Stefan Becker*[b].

[a] *Present address: Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania "Luigi Vanvitelli", 81100 –Caserta, Italy;* [b] *Department for NMR based Structural Biology, Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, 37077 Göttingen, Germany;* [c] *Friedrich-Schiller-University Jena, Institute of Biochemistry and Biophysics, Philosophenweg 12, 07743 Jena, Germany;*
luigi.russo2@unina2.it

STAT6 belongs to a family of transcription factors known as the signal transducers and activators of transcription (STAT). STAT family members share a similar protein structure, which is essential for their activation and function. STAT proteins mediate signaling from activated cytokine receptors to the nucleus(1). After phosphorylation at a specific tyrosine by a receptor associated Janus kinase, STATs form homo- or heterodimers and translocate into the nucleus where they modulate transcription by specific DNA sequence elements (1).STAT6 becomes activated in response to IL-4 and IL-13 and mediates most of the gene expression regulated by these cytokines. By direct interaction with specific parts of its transactivation domain, STAT6 recruits the co-activators p300/CDP and NCoA1 (also called steroid receptor coactivator-1, SRC-1), which are essential for transcriptional activation by IL-4 (2). In particular, the interaction between STAT6 and NCoA1 is modulated by a short region of the transactivation domain that includes the motif LXXLL (where X is any amino acid). The crystal structure of a STAT6-derived peptide (Leu^{794}-Gly^{814}) in complex with the NCoA1 PAS-B $domain^{257-385}$ revealed that the Leucine side-chains of the motif (Leu^{802}, Leu^{805} and Leu^{806}), are deeply embedded into a hydrophobic groove of the surface of NCoA1 (3). More recently, it has been demonstrated by a fluorescence polarization binding assay that additional residues (Leu^{794}, Pro^{797} and Thr^{798}), flanking the LXXLL motif in STAT6, play an important role in stabilizing the protein binding to NCoA1 (4). Here, we report the structural characterization of the complex between a STAT6-derived peptide encompassing the region from Gly^{783} to Gly^{814} and the NCoA1 PAS-B $domain^{257-385}$ using Nuclear Magnetic Resonance (NMR) and X-ray crystallography. The structural characterization of the $STAT6^{783-814}$/$NCoA1^{257-385}$complex demonstrates that $STAT6^{783-814}$peptide binds the NCoA1 PAS-B $domain^{257-385}$ by additional amino acid interactions from its N-terminal region resulting in a more extended binding interface with NCoA1 compared to that identified before in the crystal structure with the $STAT6^{794-814}$ peptide.

References: 1. X. Xu, Y.L. Sun, T. Hoey Science, 1996, 273, 794-797. 2. C.M. Litterst, E. Pfitzner J. Biol. Chem., 2001, 276, 45713-45721. 3. A. Razeto, V. Ramakrishnan, C.M. Litterst, K. Giller, C. Griesinger, T. Carlomagno, N. Lakomek, T. Heimburg, M. Lodrini, E. Pfitzner, S. Becker J. Mol. Biol., 2004, 336, 319-329. 4. M. Seitz, L.T. Maillard, D. Obrecht, J.A. Robinson ChemBioChem, 2008, 9, 1318-1322.

How can work methanol dehydrogenase from Methylacidiphilum fumariolicum with the alien Ce(III) ion in the active center? A theoretical study

Mario Prejanò[a], *Tiziana Marino*[b], *Nino Russo*[a].

[a] *Dipartimento di Chimica e Tecnologie Chimica, Università della Calabria, Via Pietro Bucci, 87036 Arcavacata, Rende CS; mario.prejano@unical.it*

La metanolo-de-idrogenasi (MDH), enzima appartenente alla classe delle ossidoriduttasi, è una metallo-proteina, generalmente calcio-dipendente, in grado di catalizzare efficientemente l'ossidazione del metanolo ed altri alcol primari.
Recentemente, una metanolo-deidrogenasi (MDH) contenente uno ione cerio, nel sito attivo, è stata isolata dal batterio *Methylacidiphilum Fumariolicum* (1). Con l'obiettivo di fare luce su come la sostituzione del metallo può influenzare il meccanismo catalitico, è stato effettuato uno studio teorico DFT comparativo tra i due metallo-enzimi, calcio e cerio dipendenti (rispettivamente, Ca-MDH e Ce-MDH).
La Superficie di Energia Potenziale (PES) ottenuta mostra come entrambi i metallo-enzimi preferiscano un meccanismo di addizione-eliminazione-protonazione; la barriera dello stato limitante la reazione per la Ce-MDH è stata calcolata pari a 19.4 kcal/mol.

References: 1. A. Pol, T. R. M. Barends, A. Dietl, A. F. Khadem, J. Eygensteyn, M. S. M. Jetten, H. J. M. Op den Camp, *Enviromental Microbiology*, 2014, *16(1)*, 255.

Aminoproline-RGD functionalized gold nanoparticles for targeting of integrins involved in tumor angiogenesis

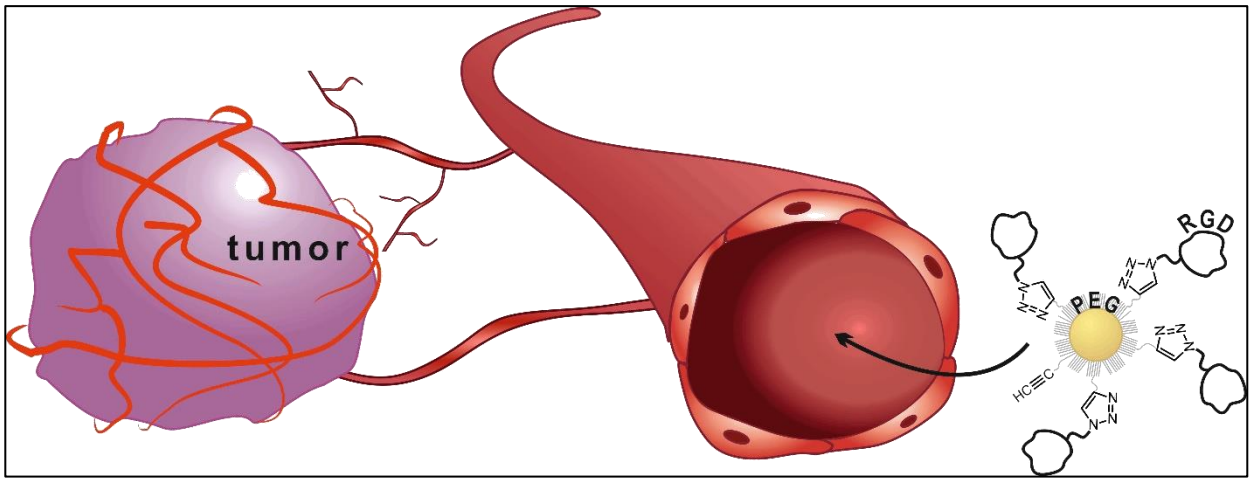
Vito Maggi[a,b], *Francesca Bianchini*[c] , *Andrea Sartori*[d] *and Roberto Fiammengo*[a].

[a]*Center for Biomolecular Nanotechnologies@UniLe, Istituto Italiano di Tecnologia (IIT), Via Barsanti,73010, Arnesano(Lecce), Italy;* [b]*Department of Engineering for Innovation, University of Salento, Via per Monteroni Km 1, 73100, Lecce, Italy;* [c]*Dipartimento di Scienze Biomediche Sperimentali e Cliniche "Mario Serio" - Università degli Studi di Firenze, Viale GB Morgagni 50 50134 Firenze;* [d]*Dipartimento di Farmacia, Università degli Studi di Parma,Viale Parco Area delle Scienze 27/a, 43124 Parma; vito.maggi@iit.it*

Integrin $\alpha_v\beta_3$ is a cell-adhesion molecule involved in angiogenesis, tumor invasion and metastasis which is overexpressed by tumor cells as well as by the endothelial cells of tumor neovasculature. The most potent $\alpha_v\beta_3$ ligands are cyclic peptides containing the RGD sequence. Ligand affinity can be further enhanced by utilizing multivalent scaffolds. Gold nanoparticles (AuNPs) could be ideal platforms for the multivalent presentation of RGD peptidomimetics targeting $\alpha_v\beta_3$ integrins aiming at theranostic formulations for tumor diagnosis and treatment.

We are developing novel PEGylated AuNPs (1) functionalized with multiple copies of cyclic-aminoproline RGD peptides (cAmpRGD) (2) which show high affinity and selectivity for $\alpha_v\beta_3$ integrins.

In this contribution we will discuss the molecular design, the preparation and characterization of these nanoparticles. Furthermore, we will show their excellent targeting properties from data collected using the human melanoma cell line M21 which overexpress integrin $\alpha_v\beta_3$. In fact, cAmpRGD-AuNPs target M21 cells 4 times more efficiently than control AuNPs as demonstrated by ICP-OES, selectively inhibit cellular adhesion to vitronectin (the natural, RGD containing ligand) by 50% at 1 nM concentration, and do not show any significant toxicity at concentrations as high as 10 nM after 24 h as demonstrated by Annexin V/ PI staining assays. We will also present bifunctional AuNPs functionalized with both cAmpRGD and a fluorophore useful in confocal microscopy imaging. cAmpRGD-AuNPs are expected to have great potential as novel multimodal (e.g. microSPECT/CT) tracers for diagnostic imaging (3).



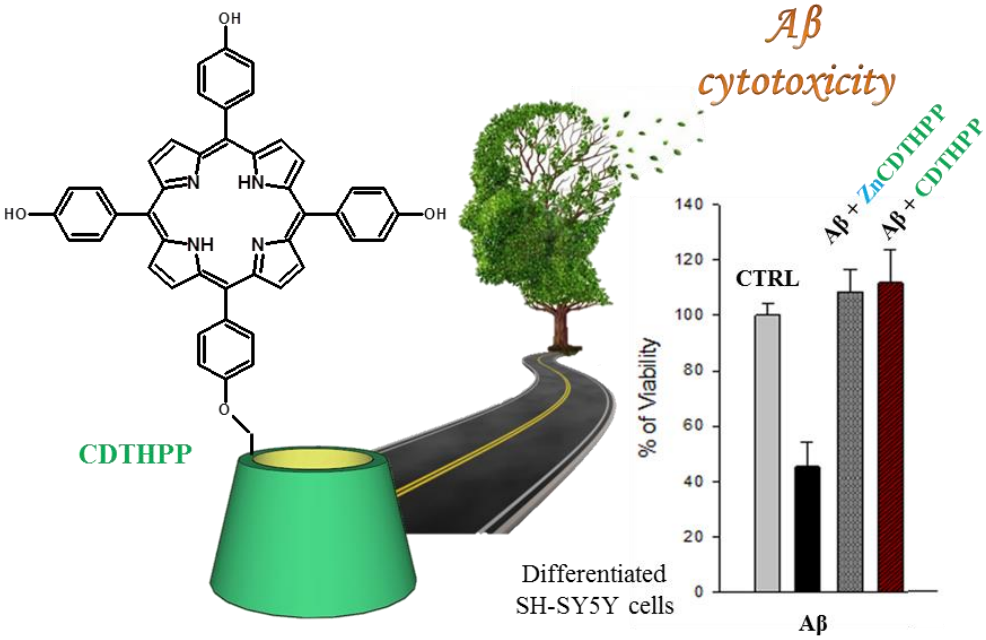
References: 1. Maus, L.; Dick, O.; Bading, H.; Spatz, J. P.; Fiammengo, R. *ACS Nano* 2010, *4*, 6617. 2.Sartori, A.; Bianchini, F.; Migliari, S. *et al. MedChemComm* 2015, *6*, 2175. 3. Kim, Y.-H.; Jeon, J.; Hong, S. H. *et al. Small* 2011, *7*, 2052.

Functionalized cyclodextrins as modulators of Aβ cytotoxicity

Valentina Oliveri[a], Stefania Zimbone[b], Maria Laura Giuffrida[b], Flora Marianna Tomasello[b], Francesco Bellia[b], Graziella Vecchio[a].

[a] Dipartimento di Scienze Chimiche, Università degli Studi di Catania, 95125 – Catania; [b] Istituto di Biostrutture e Bioimmagini, CNR, 95126–Catania; E-mail oliveri; valentina22@gmail.com

Aggregation of Amyloid-beta (Aβ) is one of the crucial events occurring during Alzheimer's disease (AD). Preventing or reducing aggregation and cytotoxicity of Aβ is one of therapeutic strategies under development or in clinical trials. Numerous studies have shown that sugars such as cyclodextrins (CyDs) provide neuroprotection in AD (1). Moreover, we have recently reported that the conjugation of cyclodextrins with aromatic moieties could provide a new avenue to the identification of novel and important modulators of Aβ aggregation (2,3,4,5). Herein, we show that a cyclodextrin compound bearing a porphyrin moiety and its zinc complex are effective in suppressing Aβ cytotoxicity. We tested the ability of the cyclodextrin-porphyrin conjugate (CDTHPP) and its zinc complex (ZnCDTHPP) to affect the toxicity of Aβ oligomers in differentiated neuroblastoma cells (SH-SY5Y). We also studied in parallel the parent compounds of the conjugates, β-cyclodextrin (CD) and 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin (THPP), to demonstrate that the conjugate activity against Aβ toxicity could arise from the synergy of the THPP and CD properties.
Dot Blot analysis, UV-vis, circular dichroism, dynamic light scattering and high-performance liquid chromatography-mass spectrometry studies were performed to investigate the nature of interaction between Aβ and the porphyrin-cyclodextrin conjugates. Finally, we took advantage of the intrinsic fluorescent properties of the derivatives to verify the cell internalization of these systems. Overall, the conjugation with cyclodextrins may be a new avenue for modulating Aβ cytotoxicity.



References: 1. Oliveri et al. (2016). Chem.-Asian J., 11, 1648. 2. Oliveri et al. (2013). Chem.-Eur. J., 19, 13946. 3. Oliveri et al. (2014). Chem.-Eur. J., 20, 8954. 4. Oliveri et al. (2015). Chem.-Eur. J., 21, 14047. 5. Oliveri et al. (2017), Chem.-Eur. J., 23, 4442.

Specific secondary interactions between ubiquitin and UBA observed in cell-mimicking crowded solution

Andrea Bortot[a], Francesca Munari[a], Serena Zanzoni[a], Mariapina D'Onofrio[a], David Fushman[b] and Michael Assfalg[a].

[a]Department of Biotechnology, University of Verona, Strada Le Grazie 15; [b]Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA; andrea.bortot@univr.it

Despite significant advancements in our understanding of ubiquitin-mediated signaling, the influence of the intracellular environment on the formation of transient ubiquitin-partner complexes remains poorly explored(1,2). In our work, we introduce macromolecular crowding as a first level of complexity toward the imitation of a cellular environment in the study of such interactions (3). Using NMR spectroscopy, we find that the stereospecific complex of ubiquitin and the ubiquitin-associated domain (UBA) is minimally perturbed by the crowding agent Ficoll. However, in addition to the primary canonical recognition patch on ubiquitin (4), secondary patches are identified, indicating that in cell-mimicking crowded solution, UBA contacts ubiquitin at multiple sites.

References: 1. Pickart CM and Eddins MJ (2004) Ubiquitin: structures, functions, mechanisms. Biochim Biophys Acta 1695, 55–72. 2. Komander D and Rape M (2012) The ubiquitin code. Annu Rev Biochem 81, 203–229. 3. Theillet F-X, Binolfi A, Frembgen-Kesner T, Hingorani K, Sarkar M, Kyne C, Li C, Crowley PB, Gierasch L, Pielak GJ et al. (2014) Physicochemical properties of cells and their effects on intrinsically disordered proteins (IDPs). Chem Rev 114, 6661–6714. 4. Varadan R, Assfalg M, Haririnia A, Raasi S, Pickart C and Fushman D (2004) Solution conformation of Lys63-linked di-ubiquitin chain provides clues to functional diversity of polyubiquitin signaling. J Biol Chem 279, 7055–7063.

ZnTPPS demetallation: role of polyelectrolytes on aggregation after protonation in acid

Massimiliano Gaeta[a], *Rosalba Randazzo*[a], *Domenico Andrea Cristaldi*[a], *Alessandro D'Urso*[a], *Roberto Purrello*[a] *and Maria Elena Fragalà*[a].

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Catania, V.le A. Doria, 6 Catania 95125 Italy; mgaeta@unict.it*

Porphyrins are very versatile compounds whose chemical-physical properties can be tuned through a careful choice of peripheral substituent groups, which are responsible of their aggregation state.(1) In particular, in the case of water-soluble porphyrins, the spatial arrangement of chromophores, through non-covalent intermolecular interactions, can be conveniently controlled acting on medium properties such as charge repulsion, ionic strength and pH. Although the self-assembly of meso-benzyl sulfonated porphyrin is mainly driven by protonation of the porphyrin core, the presence of a metal in the porphyrin core can strongly influence the aggregation pathway.(2,3)
ZnTPPS is one of the most studied metalloporphyrins, because of the importance of zinc in biology, but also for its application in photocatalysis. Therefore, the study of its demetallation and aggregation tendency is fundamental to better understand the control of porphyrin stability (in acid media) in photocatalysis, sensing, DSSC, photodynamic therapy and many other bio- and nanotechnological fields.
Herein we investigate the behaviour of ZnTPPS at different pH values and, in particular, we study ZnTPPS demetallation(4,5) in aqueous solution and related aggregation of the demetallated/protonated forms (H_2TPPS^{4-}, H_4TPPS^{2-}) in presence of anionic and cationic polyelectrolytes. In this respect the interactions with Poly-D-Glutamate (PDG) and Poly-L-Lysine (PLL), modulated by system electrostatics and by the presence of axially coordinated central metal, trigger both protonation occurrences as well as porphyrin self-aggregation.
Herein, a detailed spectroscopic analysis in order to better understand the crucial role of electrostatic interactions experienced by metallated inner core in strong acid solution has been performed. The obtained results point to a significant role of polylysine on overall demetallation/protonation process: in fact, this cationic polypeptide makes less accessible the metal core of the porphyrin, involving a slower demetallation process, but at the same time it catalyzes formation of J-aggregates (Fig.1).

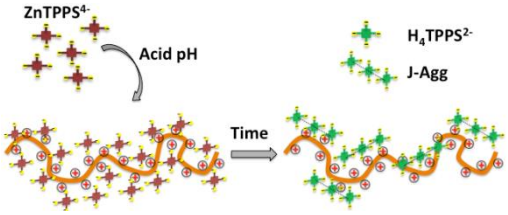


Fig.1: Templating action of the PLL on the J-aggregate formation from ZnTPPS in acidic conditions

References: 1. Chen Z., Lohr A., Saha-Moller C. R. and Wurthner F., *Chemical Society Reviews*, 2009, 38, 564-584.2. Romeo A., Castriciano M.A., Zagami R., Pollicino G., Monsù Scolaro L. and Pasternack R.F. *Chem. Sci*. 2017, 8, 961-967. 3. Purrello R., Bellacchio E., Gurrieri S., Monsù Scolaro L., Raudino A., Lauceri R. and Santoro A.M. *J. Phys. Chem. B* 1998, 102, 8852-8857. 4. Farajtabar A., Gharib F., Jamaat P. and Safari N.; *J. Chem. Eng. Data* 2008, 53, 350-354. 5. Wang X., Zhao L., Ma R., An Y. and Shi L., *Chem. Commun.* 2010, 46, 6560-6562.

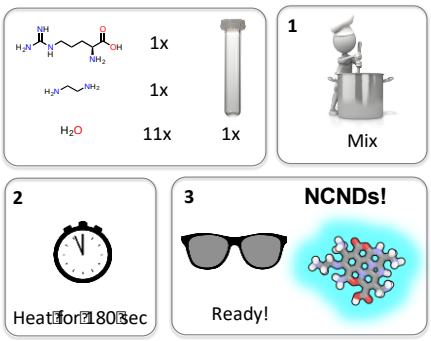
Synthesis, Separation and Characterization of Small and Highly Fluorescent Nitrogen-Doped Carbon NanoDots

Francesca Arcudi[a] *and Maurizio Prato*[abc].

[a] *Dept. of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, University of Trieste, Trieste, Italy;* [b]*Carbon Nanobiotechnology Laboratory, CIC biomaGUNE, Donostia-San Sebastian, Spain;* [c] *Basque FdnSci Ikerbasque, Bilbao 48013 (Spain); farcudi@units.it*

Extensive effort has been devoted to obtain non-toxic fluorescent nanomaterials, as an alternative to the popular semiconductor-based quantum dots (QDs). Carbon nanodots (CNDs) are recently discovered nanocarbons that comprise discrete, quasispherical nanoparticles with size below 10 nm and they have gradually become a prominent new member of the nanocarbon family. Compared to traditional semiconductor QDs and organic dyes, photoluminescent CNDs are potentially superior in terms of biological properties, high (aqueous) solubility, robust chemical inertness, facile modification and high resistance to photobleaching. A number of different synthetic protocols have been developed and reported (1). However, the structure and size of CNDs are still difficult to control. Therefore, a simple and cost-effective process, giving high quality and homogeneous nanodots remains a challenge.

Herein, we report a facile bottom-up approach to carbon nanodots (CNDs), using a microwave-assisted protocol under controlled conditions (2). Amino acids have been used as precursors due to their abundant, inexpensive, biocompatible and eco-friendly nature. The as-prepared nitrogen-doped CNDs (NCNDs) show narrow size-distribution, abundant surface traps and functional groups, resulting in tunable fluorescent emission and excellent solubility in water. Moreover, we present a general method for the separation of NCNDs by low-pressure size-exclusion chromatography, leading to an even narrower size distribution, different surface composition and optical properties. They display among the smallest size and the highest FLQYs reported so far. ^{13}C-enriched starting materials produced N^{13}CNDs suitable for thorough NMR studies, which gave useful information on their molecular structure. Moreover, they can be easily functionalized and can be used as water soluble carriers. This work provides a new avenue to size, surface controllable, structurally defined CNDs towards tailored properties for specific applications (3,4).



References: 1. S. Y. Lim, W. Shen, Z. Gao *Chem. Soc. Rev.* 2015, *44*, 362–381. 2. Arcudi, F.; Đorđević, L.; Prato, M. *Angew. Chem. Int. Ed.* 2016, *55*, 2107–2112. 3. Arcudi, F.; Đorđević, L.; Prato, M. *Angew. Chem. Int. Ed.* 2017, *56*, 4170-4173. 4. Carrara, S.; Arcudi, F.; Prato, M., De Cola, L. *Angew. Chem. Int. Ed.* 2017, *56*, 4757-4761.

Peptide Targeted Gold Nanostructures for high effective SERRS Imaging of Colorectal Cancer Cells

Marina Gobbo[a], Francesca Biscaglia[a], Senthilkumar Rajendran[b], Clara Benna[b], Gianfranco Bocchinfuso[c], Paolo Conflitti[c], Lucio Litti[a] , Roberta Sommaggio[b] , Donato Nitti[b] , Antonio Rosato[b], Antonio Palleschi[c], Simona Mocellin[b] and Moreno Meneghetti[a].

[a] University of Padova, Dept. of Chemical Sciences, Padova, Italy; [b]University of Padova, Dept. of Oncological and Surgical Sciences, Padova, Italy; [c]University of Rome Tor Vergata , Dept. of Chemical Sciences & Technologies, Roma, Italy; marina.gobbo@unipd.it

Plasmonic nanoparticles are increasingly utilized in biomedical applications including imaging, diagnostics and therapy. Gold nanoparticles (AuNP), besides displaying useful optical properties, possess a facile surface chemistry and absence of inherent toxicity, an essential requirement for biological application. AuNP can passively target tumors by the enhanced permeability and retention effect, but active targeting by proteins (antibodies), peptides or small molecules, can further improve the pharmacokinetic and pharmacodynamics profiles of these multifunctional agents. The dodecapeptide YHWYGYTPQNVI (GE11) was recently identified as a specific ligand for the Epidermal Growth Factor Receptor (EGFR), which is overexpressed in many types of cancer (1). In the present work we have employed the enormous sensitivity of the Surface Enhanced Raman Resonance Scattering (SERRS) spectroscopy (2) to study the targeting activity of GE11-functionalized plasmonic nanostructures on different types of tumor cells. Nanoparticles were prepared, without stabilizing molecules, by laser ablation of a gold target in water, functionalized with a SERRS reporter (3), and conjugated with a number of ligands: mPEG, GE11 and different PEG-GE11 conjugates to study different aspects that can influence EGFR recognition. Full characterization of the nanostructures was performed by a combination of different techniques (TEM, UV-vis-NIR, DLS, Raman, etc). Nanoaggregates covered with PEG or with the monoclonal antibody Cetuximab were used as negative and positive control, respectively. Targeting of nanostructures to colorectal cancer cells, expressing or not EGFR, was checked recording the SERRS signals cell by cell, following incubation with the AuNP. The overall results show that a proper presentation of the targeting peptide on the surface of AuNP is very important to achieve high selectivity and sensitivity in colorectal cancer cells detection, and that the activity can be greater than that obtained using a specific antibody as targeting unit. This finding opens interesting perspectives in cancer theragnostic where the intense and characteristic signals of SERRS reporters can be used for tumor imaging and the strong absorption in the NIR spectral region of AuNP clusters allows to undertake a photothermal therapeutic approach to beat the tumor (4).

References: 1. Z. Li, R. Zhao, X. Wu, Y. Sun, M. Yao, J. Li, Y. Xu, J. Gu, (2005) *FASEB J. 19*,1978. 2. J. J. Giner-Casares, M. Henriksen-Lacey, M. Coronado-Puchau, L. M. Liz-Marzan, (2016) *Materials Today 19*, 19. 3. M. Meneghetti, A. Scarsi, L. Litti, G. Marcolongo, V. Amendola, M. Gobbo, M. Di Chio, A. Boscaini, G. Fracasso, M. Colombatti *Small 8*, 3733 (2012). 4. N. Frazier, H. Ghandehari (2015) *Biotechnology and Bioengineering 112*, 1967.

Investigation of the iron(II) release mechanism from human ferritin as a function of pH

Davide Sala[a], Silvia Ciambellotti[a], Andrea Giachetti[a], Paola Turano[a,b], Antonio Rosato[a,b].

[a] Centro di Risonanza Magnetica (CERM), Università di Firenze, via Luigi Sacconi 6, 50019, Sesto Fiorentino; [b] Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto Fiorentino; d.sala1388@gmail.com

Human ferritins are 24-mer nanocage structures that self-assemble from 4-helix bundle subunits. The resulting structure has octahedral symmetry. The eight C3 channels are formed by three symmetry-related motifs, specifically helix α4-loop-α3, from as many chains. Furthermore, they have been identified as the entry points of iron(II) ions. Instead, the iron release mechanism in biomineralized ferritins is less characterized.
Our kinetic measurements showed a distinct pH dependence of iron release. Lowering the pH to 4.0 resulted in significantly faster discharge of iron, accompanied by an increase of the total amount of released ions. Our MD simulations provide a detailed atomic-level view of the mechanism of iron(II) release at pH 4, which occurs through the C3 channels.
Within each individual channel, two nearby rings formed by symmetry-related Asp and Glu sidechains define the binding site to which iron ions are rapidly attracted from the internal cavity by the electrostatic gradient. Before the iron ion actually reaches the C3 site, the Asp sidechains move apart thereby allowing it to get inside the channel, coordinated by three Glu sidechains. Subsequently, the iron ion switches from three to two glutamate sidechains coordination. These two glutamates are positioned below two histidine residues, close enough to generate a salt bridge with them (Figure 1). About 5 ns before the release of the iron ion, the lifetime of the hydrogen bonds becomes significantly longer, resulting in two strictly related effects. First, a partial compensation of the negative electrostatic charge of the carboxylates that coordinate the iron ions. Second, the reinforcement of the correlation between protein dynamics and the movement of the Glu sidechains, which in turn causes an increase of the distance between the Glu sidechains. These two synergic events weaken the interaction between the metal ion and the carboxylate oxygen atoms (Figure 1). Eventually, the iron ion escapes the C3 binding site and diffuses into the bulk solution.

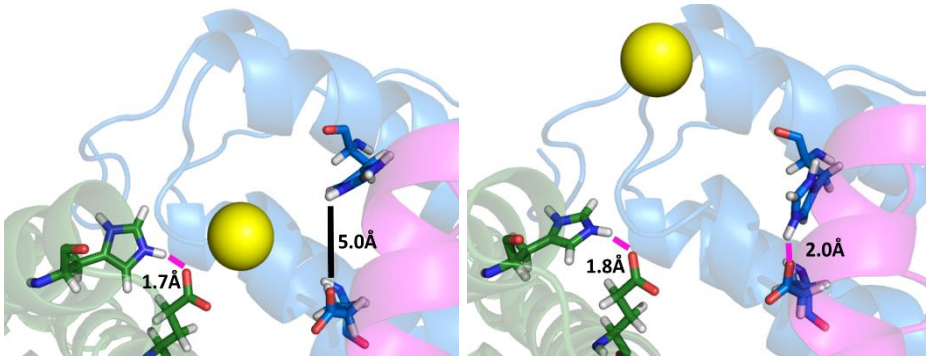


Fig. 11 Iron release after the formation of two Glu-His salt bridges.

Unveiling a VEGF-mimetic peptide sequence in IQGAP1 protein

Domenica Capasso[a], Sonia Di Gaetano[b], Veronica Celentano[b], Donatella Diana[b], Luisa Festa[b], Rossella Di Stasi[b], Lucia De Rosa[b], Roberto Fattorusso[c], Luca D. D'Andrea[b].

[a]Dipartimento di Farmacia, Università di Napoli "Federico II", Via Mezzocannone 16, Napoli, Italy; [b]Istituto di Biostrutture e Bioimmagini, CNR, Via Mezzocannone 16, Napoli, Italy; [c]Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Università della Campania "Luigi Vanvitelli", Via Vivaldi 43, 81100 Caserta, Italy: domenica.capasso@unina.it

The ability to modulate angiogenesis by chemical tools has several important applications in fields such as medicine, biology, biomaterial science (1). In this context, vascular endothelial growth factor (VEGF) and its receptors have emerged as the main regulators of physiological and pathological angiogenesis. In the last years, much focus has been paid on the search of novel molecules with antiangiogenic activity and only few artificial proangiogenic molecules have been described. In 2005, we described a proangiogenic peptide, QK, which was designed on the N-terminal α-helix of VEGF (2). This peptide binds to and activates VEGFR2, regulates VEGF receptor and NP1 gene expression and shows a bioactivity spectrum similar to VEGF (3). In the perspective of finding novel proangiogenic molecules, we searched peptide sequences with a profile similar to QK. We found that residues 1617-1627 of the GTPase activating protein (IQGAP1) shows molecular features as QK peptide sequence. IQGAP1 is a protein that belongs to a ubiquitous expressed conserved family of scaffolins implicated in different biological processes and among the various binding partners described in literature, it was demonstrated that IQGAP1 associates with the intracellular domain of VEGFR2. In this work, we characterized the bioactivity and the structural properties of the IQGAP1-derived synthetic peptide. Structural and binding features of the peptide were analysed by means of NMR spectroscopy. The biological activity of the novel peptide was analysed on endothelial cells. The results showed that IQGAP1-derived synthetic peptide has an activity similar to VEGF and could be considered a novel tool for reparative angiogenesis.

References: 1. L. D. D'Andrea, A. Romanelli, R. Di Stasi and C. Pedone, Dalton Trans, 2010, 39, 7625-7636. 2. L. D. D'Andrea, G. Iaccarino, R. Fattorusso, D. Sorriento, C. Carannante, D. Capasso, B. Trimarco and C. Pedone, Proc Natl Acad Sci U S A, 2005, 102, 14215-14220. 3. F. Finetti, A. Basile, D. Capasso, S. Di Gaetano, R. Di Stasi, M. Pascale, C. M. Turco, M. Ziche, L. Morbidelli and L. D. D'Andrea, Biochem Pharmacol, 2012, 84, 303-311.

Metabolomics studies of allelopathy: unravelling chemical interactions between Mediterranean plants through an omics approach

Monica Scognamiglio and Bernd Schneider.

Max Planck Institute for Chemical Ecology, Research Group Biosynthesis/NMR, Hans-Knoell-Str. 8, 07745 Jena, Germany; mscognamiglio@ice.mpg.de

Allelopathy plays a very important role in natural and agricultural ecosystems and it has been suggested to have a great impact on vegetation of Mediterranean area (1). It is defined as any direct or indirect, harmful or beneficial effect of one plant on another through the production of chemicals released into the environment (2).
The understanding of this phenomenon has been partially constrained, among other things, by the methods available to study the secondary metabolites involved. A new method based on metabolomics has been recently developed (3, 4), and it is herewith applied to the study of allelochemicals from selected plant species of the Mediterranean region. Donor plant (*Arbutus unedo*, *Myrtus communis*, *Medicago minima* and *Daphne gnidium*) extracts were analysed by ^{1}H and 2D NMR in order to define their chemical composition. They were tested for their phytotoxicity on a receiving plant species (*Aegilops geniculata*). Morphological and metabolomics analyses were carried out on shoots and roots of *A. geniculata* plants treated with the extracts. Tests were carried out also with partially purified fractions and with the pure putative allelochemicals. The extracts of the four plant species showed a strong inhibitory activity on the receiving plant. NMR paired with multivariate data analysis of the receiving plant let to hypothesize the main metabolic pathways affected. Studies with the pure compounds confirmed in some cases the putative allelochemicals, while in other cases it was possible to determine the occurrence of synergistic effects. Some of the compounds were taken up and, in some cases, modified by the receiving plant.
The metabolomics approach proved to be a very useful tool for these studies.
Although phytotoxic activity is only one aspect of allelopathy, the identification of the active compounds lays the bases for in field studies, while the identification of the metabolic pathways affected by the allelochemicals offers new insights for the study of their mode of action.

References: 1. Muller, C. H., 1969. Plant Ecol 18, 348-357. 2. Rice E. L., Allelopathy, 1984. 3. D'Abrosca B. et al., 2013. Phytochemistry 93, 27-40. 4. Scognamiglio M. et al., 2014. Phytochemistry 106, 69-85.

Targeting of the G-quadruplex-forming bcl2G4-1 region in the human Bcl-2 gene with Peptide Nucleic Acid: an anti-gene approach for cancer treatment.

Andrea P. Falanga[a], *Nicola Borbone*[a], *Stefano D'Errico*[a], *Brunella Pinto*[a], *Maria Marzano*[a], *Gennaro Piccialli*[a] *and Giorgia Oliviero*[b].

[a] *University of Naples "Federico II", Department of Pharmacy, Via D. Montesano 49, 80131 - Naples, Italy;*
[b] *University of Naples "Federico II", Department of Molecular Medicine and Medicinal Biotechnology, Via Pansini 5, 80131 - Naples, Italy; and.falanga@gmail.com*

Human Bcl-2 gene contains GC-rich regions upstream of the P1 promoter that are involved in the regulation of Bcl-2 gene expression. In this region Guanine-rich DNA sequences fold in quadruplex structures under physiological concentrations of K^+. G-quadruplexes are found throughout significative regions of human genome, for example promoters of oncogenes, such as Bcl-2 of which, the abnormal overexpression is associated with many human tumours. Several oligonucleotides (ON) and ON analogues are employed as tools to counteract the expression of this oncogene. Among these the Peptide Nucleic Acids (PNAs) are the most promising. PNAs are mimic of DNA in which the back-bonds sugar-phosphate are replaced by a ethylamine glycine moiety, due these characteristic they can form, with DNA target, some structures more stable than the natural DNA/DNA complexes (1-6). To down-regulate anti-apoptotic Bcl-2 oncoproteins, here we propose an anti-gene approach based on PNA oligomers, allowing to target the bcl2G4-1 DNA sequence. Structural interactions towards the DNA target have been investigated by chemical-physical techniques. PNAs can interact with the DNA target, as shown by Circular Dichroism (CD), CD-melting and PAGE studies. Furthermore, the ability of these molecules to cross cell membranes has been studied. PNAs are able to elicit their action only when enter cell nuclei. Fluorescence microscopy also demonstrated that the suitably-FITC-labeled oligomers, specifically cross membrane and enter cell nuclei of tumor cells. These findings indicate the potential of novel PNA-based approach for the cancer therapy. This approach holds promise to improve a site specific and safe chemotherapy, reducing the unwanted toxicity to healthy tissues and organs.

References: 1. Brown, S.C., Thomson, S.A., Veal, J.M. and Davis, D.G., NMR solution structure of a peptide nucleic acid complexed with RNA. Science, 265 (1994) 777. 2. Rasmussen, H., Kastrup, J.S., Nielsen, J.N., Nielsen, J.M. and Nielsen, P.E., Crystal structure of a peptide nucleic acid (PNA) duplex at 1.7 A resolution. Nat. Struct. Biol., 4 (1997) 98. 3. Leijon, M. et al., Structural characterization of PNA-DNA duplexes by NMR. Evidence for DNA in a B-like conformation. Biochemistry, 33 (1994) 9820. 4. Eriksson, M. and Nielsen, P.E., Solution structure of a peptide nucleic acid-DNA duplex. Nat. Struct. Biol., 3, (1996) 410. 5. Betts, L., Josey, J.A., Veal, J.M. and Jordan, S.R., A nucleic acid triple helix formed by a peptide nucleic acid-DNA complex.Science,270 (1995) 1838. 6. Amato, B. Pagano, N. Borbone, G. Oliviero, E. De Pauw, S. D. Errico, V. Piccialli, M. Varra, C. Giancola, G. Piccialli, L. Mayol, S. Naturali, N. Federico, D. Montesano, and F. Sa, "Targeting G-Quadruplex Structure in the Human c-Kit Promoter with Short PNA Sequences," pp. 654–663, 2011.

Peptaibols: naturally occurring peptides as biopesticides

Marta De Zotti[a], Alessandro Bortolotto[a,b], Ibrahim Elmaghraby[b], Luca Sella[b] and Francesco Favaron[b].

[a] Department of Chemistry, University of Padova, Via Marzolo 1, 35131 Padova; [b] Department of Land, Environment, Agriculture and Forestry, Viale Dell'Universita' 16, 35010 Legnaro (Padova); marta.dezotti@unipd.it

Fungi belonging to the genus *Trichoderma* are distributed worldwide and have been used successfully in field trials against many crop pathogens. They produce peptaibols, a peculiar family of peptides, as part of their defense system against other microorganisms. Such secondary metabolites are known for their plant-protection properties: they (i) possess antimicrobial activity, (ii) act as stimulants of plant defences and growth (iii) elicit plant production of volatiles to attract natural enemies of herbivorous insects. Moreover, peptides are ecofriendly compounds that are degraded by enzymes to nontoxic amino acids. With this presentation, we show our progress towards the exploitation of naturally occurring peptides of the peptaibols family as biopesticides. With such compounds, we can circumvent both the health hazards and the unreliable effectiveness in open field connected with the use of antagonistic microorganisms as biological control agents, while keeping the biomolecules responsible for their beneficial effects. Our peptides have been tested (alone or in combination) *in vitro* against the fungi *Botrytis cinerea* and *Penicillum italicum* and the bacterium *Pectobacterium carotovorum*, some of them considered priority pests for fruits, vegetables and medicinal plants across European countries. We found that an analog of the peptaibol trichogin is able to completely inhibit the growth of *B. cinerea* for over a week at low micromolar concentrations.

Comunicazioni Poster

PASTA sequence composition as a footprint of protein class identity

Luisa Calvanese[a], Lucia Falcigno[a,b,c], Flavia Squeglia[c], Rita Berisio[c] and Gabriella D'Auria [a,b,c].

[a]CIRPeB, University of Naples Federico II, via Mezzocannone 16, 80134, Naples (IT). [b]Department of Pharmacy, University of Naples "Federico II", via Mezzocannone 16, 80134, Naples (IT). [c]Institute of Bio-structures and Bio-imaging- CNR, via Mezzocannone, 16, 80134, Naples (IT); gabriella.dauria@unina.it

PASTA domains are small modules expressed in bacteria and found in one or multiple copies at the C-terminal end of several Penicillin Binding Proteins (PBPs) and Ser/Thr protein kinases (STPKs) (1,2,3). Currently, the functional role of PASTA is not yet completely understood. At present, PASTA is annotated as a sensor domain. It has been proposed that its binding to opportune ligands, i.e. muropeptides, is able to activate the cognate proteins to their functions. However, some experimental data proved that such role might not be a general property of PASTA. Even though sharing identical folds, several studies made clear that PASTAs from different protein classes do not share the same functions. In reason of their capacity to bind cell wall fragments, PASTAs from STPKs were proposed as sensor domains for the cognate kinases. The same function associated to PASTAs from PBPs has been considered reliable until few years ago, when the binding ability *vs* cell wall fragments or their mimics did not pass the experimental verifications (4,5). For that, even though a sensor function cannot yet be discarded, it was hypothesized that PASTAs in PBPs might have a role as structure stabilizer (5,6).

A search in the PASTA PFAM family (PF03793) results in 11049 sequences, 79 architectures and 47 structures. Proteins containing PASTA domains are mostly distributed in Actinobacteria and Firmicutes, *phyla* that include some of the most dangerous microorganisms for human health like *Mycobacterium tuberculosis* (*Mtb*) and *Staphylococcus aureus* (*Sa*). Their external localization, the linking to enzymes essential for bacteria metabolisms and the fact that they are not expressed in eukaryotes, make PASTA interesting targets for new antibiotics drugs (1). PASTA domains, belonging or not to different protein classes, show wide ranges of sequences identities. Amino acid compositions, total charges and distribution of the hydrophobic/hydrophilic patches on the surface, significantly vary among PASTAs from STPKs and PBPs and seem to correlate with different functions, such as the ability/not ability to bind muropeptide (7). Here we show the analysis of amino acid composition performed on all PASTA sequences from PBPs and STPKs reported for Actinobacteria and Firmicutes in the PFAM database.

References: 1. Yeats, C.; Finn, R.D.; Bateman, A. *Trends Biochem Sci*, 2002, *27*, 438. 2. Goffin, C.; Ghuysen, J.M. *Microbiol Mol Biol Rev*, 2002, *66*, 702-738, table of contents. 3. Dworkin, J. *Curr Opin Microbiol*, 2015, *24*, 47-52. 4. Calvanese, L.; Falcigno, L.; Maglione, C.; Marasco, D.; Ruggiero, A.; Squeglia, F.; Berisio, R.; D'Auria, G., *Biopolymers*, 2014, *101*, 712-719. 5. Maurer, P.; Todorova, K.; Sauerbier, J.; Hakenbeck, R. *Microb Drug Resist*, 2012, *18*, 314-321. 6. Calvanese, L.; Falcigno, L.; Squeglia, F.; D'Auria, G.; Berisio, R. *J Biomol Struct Dyn*, 2016, 1-8. 7. Calvanese, L.; Falcigno, L.; Squeglia, F.; D'Auria, G.; Berisio, R. *Curr. Med. Chem.*, 2017, 24, DOI: 10.2174/0929867324666170216112746.

Miniaturizing VEGF: Peptides mimicking the discontinuous VEGF receptor-binding site modulate the angiogenic response

Sara Auriemma[a], Lucia De Rosa[b], Federica Finetti[c], Donatella Diana[d], Rossella Di Stasi[b], Alessandra Romanelli[c], Roberto Fattorusso[d], Marina Ziche[e], Lucia Morbidelli[e], Luca Domenico D'Andrea[b]and Giuseppe D'Aiello[a].

[a] ITI Galvani, Giugliano; [b]Institute of Biostructure and Bioimagining, CNR, Napoli, [c]Italy ,Faculty of Pharmacy , University of Naples ''Federico II'; [c]Faculty of Environmental Sciences , [d]Seconda Università degli Studi di Caserta; [e]Department of Pharmacological Science , University of Siena – Italy; saraauriemma@libero.it

Angiogenesis is a physiological process during which new capillaries sprout from existing vessels but, when pathological, it contributes to the development of different types of tumors, and to the birth of metastases. VEGF, the main growth factors, plays a significant role in the the *angiogenic switch* (1) process. As part of this VEGF binds with high affinity two tyrosine kinase receptors Flt-1 and KDR (2). Three are the main interacting points of the VEGF with its own receptors: It consist in a discontinuous surface which comprises binding residues distributed in three regions belonging to both VEGF monomers (3): the N-terminal helix (residues 17-25), the loop joining strand β3 and β4 (residues 61-66) of one VEGF monomer, and the β-hairpin encompassing strand β5 and β6 (residues 79-93) of the other VEGF monomer. In order to find new active biomolecules which can modulate the interaction of VEGF discontinuous region (4) with their own receptors, we designed and synthesized a set of peptides mimicking the two secondary structure elements of VEGF α-helix (17-25) and β-hairpin (79-93) involved in the receptor recognition. The two linear amino acid segments were synthesized by solid-phase synthesis and conjugated by *native chemical ligation* (NCL) (5) through amino acid spacers of variable length and flexibility. They were analyzed by CD, NMR; LC-MS. Their biological activity has been investigated by *in vitro* and *in vivo* assays, highlighting a VEGF-like biological activity.

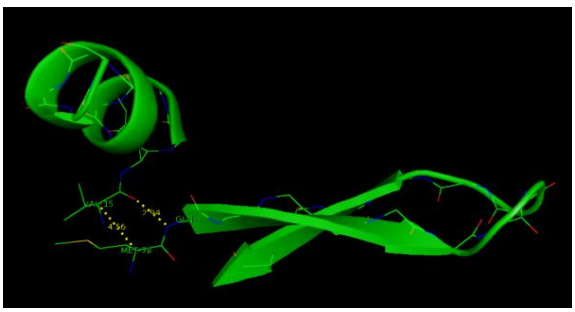


Figure 1: Molecular detail of VEGF structure highlighting the proximity between the a-helix (17-25) and the β-hairpin (79-91) of VEGF. Secondary structure element is represented as ribbon. The distance between the different aminoacids are reported in yellow

References: 1. Camerliet, P. *Nat. Med.* 9, 2003, 653. 2. Camerliet, P. *Nat. Med.* 7, 2001, 575. 3. Wiesmann, C., Fuh, G., Christinger, H.W., Eigenbrot, C., Wells, J.A and de Vos, A., *Cell* 91, 1997. 4. L. Nevola and E. Giralt, *Chemical communications*, 2015, 51, 3302-3315. 5. DP. E. Dawson, T. W. Muir, I. Clark-Lewis and S. B. Kent ,*Science*, 1994, 266, 776-7.

Folding mechanisms steer amyloid fibrils formation propensity of prokaryotic zinc finger domains

Gianluca D'Abrosca [a], *Gaetano Malgieri* [a], *Maddalena Palmieri* [a], *Luciano Pirone* [b], *Luigi Russo* [a], *Michele Francesco Maria Sciacca* [c], *Rosarita Tatè* [d], *Valeria Sivo* [a], *Ilaria Baglivo* [a], *Roksana Majewska* [a], *Paolo Vincenzo Pedone* [a], *Carla Isernia* [a], *Mario De Stefano* [a], *Emilia Maria Pedone* [b], *Danilo Milardi* [c], *and Roberto Fattorusso*[a].

[a] *Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Via Vivaldi 43, 81100 Caserta (Italy);*
[b] *Institute of Biostructures and Bioimaging-CNR, Via Mezzocannone 16, 80134 Naples (Italy);*
[c] *Institute of Biostructures and Bioimaging-CNR, Viale A. Doria 6, 95125 Catania (Italy);*
[d] *Institute of Genetics and Biophysics "Adriano Buzzati-Traverso"-CNR, Via P. Castellino 111, 80131 Napoli (Italy);*
gianluca.dabrosca@unicampania.it

We describe the amyloidogenic propensities of three iso-structural globular proteins belonging to the prokaryotic zinc finger family (1) that possess different folding mechanisms. Particularly, the metal-free $Ml4_{52–151}$ (2) folds via classic two-state cooperative transition while the metal-binding homologues, Ros87 (2) and $Ml1_{53-149}$, exhibit more complex folding pathways, including a barrier-less downhill scenario. The results, obtained by CD and fluorescence spectroscopies, DLS, transmission and scanning electron microscopies, show that within 168 hours amyloid formation has already started in Ros87, while $Ml1_{53-149}$ has formed only amorphous aggregates and $Ml4_{52–151}$ is still monomeric in solution. Overall, this study shows how different folding mechanisms, here induced by metal binding, significantly affect amyloid fibril formation propensity of highly homologous proteins.

References: 1. Malgieri, G.; Palmieri, M.; Russo, L.; Fattorusso, R.; Pedone, P. V.; Isernia, C., The prokaryotic zinc-finger: structure, function and comparison with the eukaryotic counterpart. *FEBS J* **2015,** *282* (23), 4480-96. 2. Palmieri, M.; Malgieri, G.; Russo, L.; Baglivo, I.; Esposito, S.; Netti, F.; Del Gatto, A.; de Paola, I.; Zaccaro, L.; Pedone, P. V.; Isernia, C.; Milardi, D.; Fattorusso, R., Structural Zn(II) implies a switch from fully cooperative to partly downhill folding in highly homologous proteins. *J Am Chem Soc* **2013,** *135* (13), 5220-8.

Covalent Functionalization of Cotton Fabric with Antimicrobial Peptides: New Synthetic Strategies

Anna Primon[a], *Marta De Zotti*[a] *and Cristina Peggion*[a].

[a] *Department of Chemistry, University of Padova, Via Marzolo 1, 35131 Padova; marta.dezotti@unipd.it*

The onset of bacterial resistance is a worldwide problem, in particular in healthcare environments. The development of antimicrobial textiles could represent an important aid in the struggle against pathogens, bacteria and viruses and may find a variety of applications (biomedical garments, protections devices, etc,). The new materials are based on an ordinary fabrics functionalized with antimicrobial chemical species through appropriate treatments. The ultimate goal is to transfer the bioactivity of the molecule to the fabric in a durable way.

As therapeutic agents, we focused on a class of antimicrobial peptides characterized by a very short sequence, which counts just four amino acids, suitably designed to be active against certain bacterial strains. The strength of these sequences, in addition to the weighted choice of hydrophobic and cationic residues constituting the peptide sequence, stems from the presence of an aliphatic chain at one end of the peptide sequence. Once the peptide has anchored itself to the bacterial surface, by means of electrostatic interactions, such lipophilic moiety acts by disrupting the bacterial membrane.

In this presentation, we illustrate how we synthesized and anchored the above described peptides on a cotton support. Among the various strategies that can be tempted for peptide anchoring, we chose the chemoselective ligation, with the formation of an oxime bond. An aldehyde function was obtained on the peptide by oxidation of a serine residue, while the oxyamine was suitably generated on the cotton support. Functionalized cotton substrates have undergone surface spectroscopy analysis such as XPS and FT-IR-ATR. The results highlighted the presence of peptides covalently linked to the surface. The biological evaluation of the functionalized cotton fibers is underway.

Synthesis, Conformational Analysis and Biophysical Properties of Medium-Length Peptaibols

Barbara Biondi[a], Marta De Zotti[b], Chiara Pignaffo[b], Lorenzo Stella[c], Annalisa Bortolotti[c], Cristina Peggion[b], Marco Bortolus[b] and Fernando Formaggio[a].

[a] ICB, Padova Unit, CNR, Department of Chemistry, University of Padova, Via Marzolo 1, 35131 Padova, Italy; [b] Department of Chemistry, University of Padova, Via Marzolo 1, 35131 Padova; [c] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", via della Ricerca Scientifica, Roma, Italy; marta.dezotti@unipd.it

Chalciporin A is a medium-length (14-residue) peptaibol isolated from a strain of *Sepedonium chalcipori* (1). The sequence of peptaibols is characterized by the presence of several, non-coded α-aminoisobutyric acid (Aib) residues and an uncommon C-terminal amino alcohol. Thanks to their helical structures, peptaibols display a relevant ability to interact with phospholipid bilayers. As a result, they often exhibit antimicrobial, antifungal or anticancer activity, although they sometimes target healthy human cells as well. Moreover, they are remarkably resistant to proteolysis so that the study of their mechanism of action is of interest to the design of new drugs.

In this communication, we report the total synthesis of chalciporin A and two analogs thereof, containing the paramagnetic, constrained, α-amino acid TOAC. The amino acid sequences of the three peptides are: Ac-Trp-Val-Aib-Val-Ala-Gln-Ala-Aib-Ser-Leu-Ala-Leu-Aib-Gln-Lol (chalciporin); Ac-Trp-Ala-Aib-Val-Ala-Gln-Ala-Aib-Ser-Leu-Ala-Leu-TOAC-Gln-Lol (TOAC13); Ac-Trp-Ala-TOAC-Val-Ala-Gln-Ala-Aib-Ser-Leu-Ala-Leu-TOAC-Gln-Lol (TOAC3,13).

We exploited a large combination of spectroscopic and biophysical techniques (including FT-IR absorption, CD, 2D-NMR, and fluorescence) to investigate the preferred conformation, membrane interaction, and bioactivity properties of the naturally occurring chalciporin A characterized by a relatively low (≈20%) proportion of the helicogenic Aib residue. In addition to the unlabeled peptide, we gained in-depth information from the study of the two labeled analogs. All three peptides were prepared using the SPPS methodology, which was however carefully adapted in the course of the syntheses of the poorly backbone reactive and side-chain delicate, TOAC containing analogs. Our results point to a largely predominant α-helical conformation and effective membrane affinity/penetration propensities, but to a modest antibacterial activity, for this amphiphilic peptaibol.

References: 1. T. Neuhof, A. Berg, H. Besl, T. Schwecke, R. Dieckmann, H. von Döhren, Chemistry Biodivers., 4, 1103 (2007).

Supramolecular necklace-like structures of Pluronic F127 combined with alpha and beta cyclodextrin for new topical formulation of acyclovir.

Cristina Di Donato[a], *Rosa Iacovino*[a], *Angel Concheiro*[b] *and Carmen Alvarez-Lorenzo*[b].

[a] *Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania Luigi Vanvitelli, Via A. Vivaldi 43, 81100 Caserta, Italy;* [b] *Departamento de Farmacia y Tecnología Farmacéutica, Universidad de Santiago de Compostela, Santiago de Compostela, Spain.; cristina.didonato@unicampania.it*

Pluronic® F127 (PF127) is a triblock copolymer of polyethylene oxide (PEO)-b-polypropylene oxide (PPO)-b-polyethylene oxide (PEO) used in drug formulation for its capability to form thermoreversible and mucoadhesive gel in aqueous media (1). Additionally, the supramolecular necklace-like inclusion complexes resulting from interaction between cyclodextrins (CDs) and polymer chains can open new ways to address drug formulation (2). Infact, these gels combine capability to solubilize hydrophobic drugs and tunable mechanical features (3). Thus, the aim of this work was to explore the effects of combining simultaneously both αCD and βCD with PF127 at various ratios on the rheological properties of the polypseudorotaxane systems and their capability to solubilize acyclovir. Acyclovir is a synthetic drug with a similar molecular structure to the purine nucleoside and it represents the most used antiviral for the treatment of Herpes Simplex Virus infections. Nevertheless, acyclovir shows a low water solubility that compromises both bioavailabilty and antiviral performance (4).

To carry out the work, dispersions of PF127 with αCD and βCD at different concentration ratios were prepared with and without acyclovir at 5%. The complexation between PF127 and CDs was evidenced by FT-IR Spectroscopy and X-ray Powder Diffraction. Furthermore, the rheological behavior of the copolymer was investigated and the resulted changes of its gelling temperature can be interpreted as the consequence of the penetration of some PPO hydrophobic groups of PF127 inside the βCD cavities. Acyclovir solubility was evaluated after addition of the drug in excess to the dispersions, which were stored under stirring for at least three days. Then, the samples were filtered and the absorbance at 252 nm was recorded. Irritance degree of the formulations was estimated by HET-CAM assay, showing a slight bleeding in chorioallantoic membrane only for the systems in which the βCD is in concentration at 4%.

These preliminary findings indicate that the proposed approach for delivery of acyclovir can improve the physicochemical properties of the drug and represent the starting point for further experiments.

References: 1. Choi, S.G.; Lee, S-E.; Kang, B-S.; Ng, C.L.; Davaa, E.; Park, J-S.. *PLoS ONE* 2014, *9*. 2. Zheng, Y.; Wyman, I.W. *Polymers* 2016, *8*, 198. 3. Simões, S.M.N.; Veiga, F.; Torres-Labandeira, J.J.; Ribeiro, A.C.F., Concheiro, A.; Alvarez-Lorenzo, C.. *Curr. Topics Med. Chem*. 2014, *14*, 494-509. 4. Mahmood, A.; Ahmad, M.; Sarfraz, R. M.; Usman Minhas, M.. *Adv. Polym. Technol.* 2016, doi:10.1002/adv.21711.

Modified β-Cyclodextrin inclusion complex to improve the physicochemical properties of Pipemidic Acid

Cristina Di Donato[a], *Rosa Iacovino*[a], *Margherita Lavorgna*[a] *and Carla Isernia*[a].

[a] *Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania Luigi Vanvitelli, Via A. Vivaldi 43, 81100 Caserta, Italy; cristina.didonato@unicampania.it*

The capability of cyclodextrins (CDs) to form inclusion complexes is correlated to their peculiar structure, with a relatively hydrophobic inner cavity that interacts with a variety of guest influencing their physicochemical properties, as a consequence of the complexation (1). In particular, modified cyclodextrins like Heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin (TRIMEB) are best known to be more soluble respect to natural CDs (2) and for this reason their use in pharmaceutical formulation is desiderable (3). In order to obtain an improvement of the low solubility and bioavailability of pipemidic acid (HPPA), a quinolone derivate used as therapeutic agent for urinary tract infection active against Gram (+) and Gram (-) bacteria (4), the drug was complexed with TRIMEB. The inclusion complex was prepared in the solid state by kneading method. The formation of the inclusion complex in the solid state was confirmed by FT-IR Spectroscopy and X-ray Powder Diffraction. The association in aqueous solutions of pipemidic acid with TRIMEB was investigated by UV-Vis Spectroscopy, the 1:1 stoichiometry was established by Job plot method (5) and the binding constants were determined considering the influence of the pH (6) by UV-Vis titration, taking into account the amphoteric nature of the drug.

Furthermore, the cytotoxic activities of HPPA and its complexation product with TRIMEB was evaluated using the MTT-assay on human hepatoblastoma cell line HepG2 and human breast adenocarcinoma cell line MCF-7, revealing a higher antitumor activity of the complex respect to the drug alone.

Results obtained indicate that the formation of the complex can improve the physicochemical properties of the guest to better its bioactivity and represent the starting point for the evaluation of new pharmaceutical formulation of HPPA.

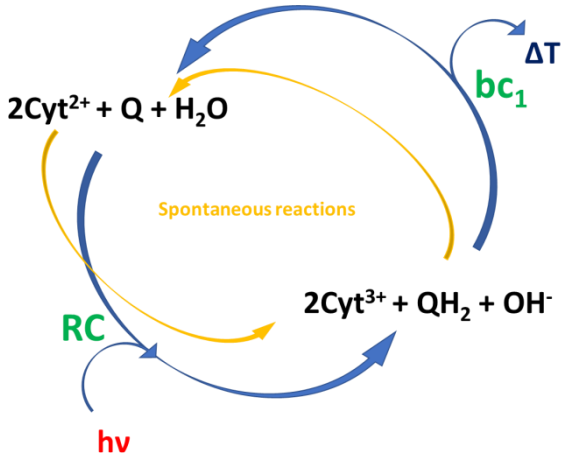
References: 1. Loftsson, T; Brewster, M. E. J. Pharm. Sci. 2012; 101: 3019-3021. 2. Iacovino, R.; Caso, J. V.; Di Donato, C.; Malgieri, G.; Palmieri, M.; Russo, L.; Isernia, C.. Curr. Org. Chem. (2016) 20: 162-176. 3. Szejtli, J.. Chem. Rev. 1998; 98: 1743-1753. 4. Iacovino, R.; Rapuano, F.; Caso, J.V.; Russo, A.; Lavorgna, M.; Russo, C.; Isidori, M.; Russo, L.; Malgieri, G.; Isernia, C.. *Int. J. Mol. Sci*. 2013, *14*, 13022-13041. 5. Huang, C.Y.. 1982; 87: 509-525. 6. Di Donato, C.; Lavorgna, M.; Fattorusso, R.; Isernia, C.; Isidori, M.; Malgieri, G.; Piscitelli, C.; Russo, C.; Russo, L.; Iacovino, R.. *Molecules*. 2016, 21, 1644-1657.

Light Transducing Protocells: reconstituting and characterizing the bc1 complex into the membrane of giant lipid vesicles.

Rosa Fiorentino [a], Emiliano Altamura [a], Francesco Milano [c], Massimo Trotta [c], Anna Ferretta [c], Tiziana Cocco [c], Pasquale Stano [d] and Fabio Mavelli [a].

[a]Chemistry Department, University Aldo Moro, Bari Italy ; [b] Institute for Physical and Chemical Processes, CNR-Bari, Italy.; [c]Department of Basic Medical Sciences Neurosciences and Sense Organs, University of Bari, Bari, Italy. [d]Department of Biological and Environmental Sciences and Technologies, University of Salento; r.fiorentino1@studenti.uniba.it

Photosynthesis is responsible for the photochemical conversion of light into the chemical energy that fuels the planet Earth. The photochemical core of this process in all photosynthetic organisms is a transmembrane protein called the reaction center (RC) (1). In purple photosynthetic bacteria a simple version of this photo-enzyme catalyzes the reduction of a quinone molecule, accompanied by the uptake of two protons from the cytoplasm and the oxidation of cyt^{2+} to cyt^{3+} from external medium. In a previous work (2), giant unilamellar vesicles (GUVs) were prepared by the phase transfer method (3) reconstituting in the lipid membrane RCs retaining the physiological orientation at 90%. These synthetic protocells (RC@GUVs) are capable of generating a photo-induced proton gradient 0.061 pH units per min across the membrane under continuous illumination and in presence of an excess of cyt^{2+} and quinone in the external solution. In this contribution, bc1 extracted both from bacteria and mitochondria are reconstituted in giant vesicle membrane (bc1@GUVs) and characterized by studying the enzymatic activity in reducing cyt^{3+} to cyt^{2+} in presence of quinole QH_2. This is a forward step towards the coupling of both RC and bc1 in in the synthetic protocells order to implement the complete photo-cycle, as shown in Figure 1:



This pave the way for the construction of more functional protocells for synthetic biology which can be ultimately harnessed to synthesize ATP(4,5).

References: 1. Allen JP, Williams JC (1998) Photosynthetic reaction centers. FEBS Lett 438(1-2):5–9. 2. Altamura E, Milano F, Tangorra RR, Trotta M, Omar OH, Stano P, Mavelli F (2017) Highly oriented photosynthetic reaction centers generate a proton gradient in synthetic protocells. Proc Natl Acad Sci USA 114(15):3837-3842. 3. Pautot S, Frisken BJ, Weitz DA (2003) Engineering asymmetric vesicles. Proc Natl Acad Sci USA 100(19):10718–10721. 4. Pohorille A, Deamer D (2002) Artificial cells: Prospects for biotechnology. Trends Biotechnol 20(3):123–128. 5. Allen JP, (2017) Design of energy-transducing artificial cells. Proc Natl Acad Sci USA 114(15): 3790-3791.

Structural studies on RcnR, a Ni(II) and Co(II) sensing transcription factor

Marta Palombo [a], *Mario Piccioli* [b], *Francesco Musiani* [a], *Michael J Maroney.*[c] *and Stefano Ciurli* [a].

[a] *Department of Pharmacy and Biotechnology, University of Bologna, Italy;*
[b] *Center for Magnetic Resonance, University of Florence, Italy;*
[c] *Department of Chemistry, University of Massachusetts, USA; marta.palombo2@unibo.it*

Escherichia coli RcnR (resistance to cobalt and nickel regulator, *Ec*RcnR), is a metal-responsive transcriptional regulator that represses the expression of the Ni(II) and Co(II) exporter proteins RcnAB by binding to their promoter site in the apo-form. A computational model of *Ec*RcnR suggests the presence of three α-helices in the monomer. Each monomer is in contact with a second protein chain via the three α-helices to form a dimer. The tetrameric oligomer is obtained by the interaction between the two helices α1 from one dimer with the corresponding helices from the second dimer (1). Protein-DNA release occurs when either Ni(II) or Co(II) binds to *Ec*RcnR. *Ec*RcnR also binds the non-cognate metal ions Cu(I) and Zn(II), which have no effect on protein-DNA interaction. Prior work has shown that Ni(II) and Co(II) are found in distinct sites: while both Ni(II) and Co(II) are bound to the N-terminal Cys35 and His64 residues, Co(II) is additionally bound to His3 (2). On the other hand, Cu(I) and Zn(II) have a solvent-exposed binding site and further coordinate protein ligands that do not include the N-terminus amine (3). A molecular model of apo-*Ec*RcnR revealed the presence of Glu34 and Glu63 in the vicinity of the Ni(II) and Co(II) binding site (1). The roles of Glu34 and Glu63 in Ni(II) and Co(II) binding and selectivity were further demonstrated using site-directed mutagenesis, X-ray absorption spectroscopy (XAS) and functional assays (4).
This work will involve a structural characterization of *Ec*RcnR by using a combination of structural biology techniques. X-ray protein crystallography will be exploited to depict, at an atomic level, the tridimensional structure of the transcriptional factor in both the apo- and metal-bound form. As a first approach, a large number of commercial crystallization screenings has been used to find initial conditions for the growth of RcnR crystals. A systematic variation of the initial crystallization parameters will be carried out, by the use of trial matrices, in order to optimize them and obtain crystals suitable for X-ray diffraction experiments. In parallel, solution paramagnetic NMR spectroscopy is being used to shed light on the coordination geometry of cognate metals at the *Ec*RcnR binding site under near-physiological conditions, in order to either corroborate or review previous results.

References: 1. Musiani, F.; Zambelli, B.; Bazzani, M.; Mazzei, L.; Ciurli, S. (2015) *Metallomics* 7:1305. 2. Iwig, J.S.; Leitch, S.; Herbst, R.W.; Maroney, M.J.; Chivers, P.T. (2008) *J. Am. Chem. Soc.* 130:7592. 3. Higgins, K.A.; Chivers, P.T.; Marone,y M.J. (2012) *J. Am. Chem. Soc.* 134:7081. 4. Carr, C.E.; Musiani, F.; Huang, H.-T.; Chivers, P.T.; Ciurli, S.; Maroney, M.J. (2017) *Inorg Chem.* doi: 10.1021/acs.inorgchem.7b00527.

Analysis of testosterone fatty acid esters in the digestive gland of mussels by liquid chromatography-high resolution mass spectrometry

Cesare Guercia, Piergiorgio Cianciullo and Cinta Porte.

Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain

Several studies have indicated that up to 70% of the total steroids detected in molluscs are in the esterified form and that pollutants, by modifying the esterification of steroids with fatty acids, might act as endocrine disrupters. However, despite the strong physiological significance of this process, there is almost no information on which fatty acids form the steroid esters and how this process is modulated. This study (a) investigates the formation of fatty acid esters of testosterone in digestive gland microsomal fractions of the mussel *Mytilus galloprovincialis* incubated with either palmitoly-CoA or CoA and ATP, and (b) assesses whether the endocrine disruptor tributyltin (TBT) interferes with the esterification of testosterone. Analysis of testosterone esters was performed by liquid chromatography–high resolution mass spectrometry (UPLC-HRMS). When microsomal fractions were incubated with testosterone and palmitoly-CoA, the formation of testosterone palmitate was detected. However, when microsomes were incubated with CoA and ATP, and no exogenous activated fatty acid was added, the synthesis of 16:0, 16:1, 20:5 and 22:6 testosterone esters was observed. The presence of 100 μM TBT in the incubation mixture did not significantly alter the esterification of testosterone. These results evidence the conjugation of testosterone with the most abundant fatty acids in the digestive gland microsomal fraction of mussels.

Structural characterization of the protein FlmC from *L. plantarum*

Gianluca D'Abrosca [a], Lidia Muscariello [a], Antonella Di Pasquale [a], Valeria Vastano [a], Margherita Sacco [a], Carla Isernia [a] and Gaetano Malgieri [a].

[a] Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Via Vivaldi 43, 81100 Caserta (Italy); gianluca.dabrosca@unicampania.it

The interest in biofilm development has increased due to the impact that this sessile form of microbial growth may have on different aspects of the human life. Exploitation of microbial biofilm has been accomplished in different fields, including bioremediation and biotechnological production processes. Contrariwise, biofilms developed by pathogens represent a serious problem for human health.

Probiotic bacteria mainly belong to the group of the lactic acid bacteria of the genus *Lactobacillus* and *Bifidobacterium*. Among these, some strains of *Lactobacillus plantarum*, one of the most predominant species in the human gut microbiota of healthy individuals, have been defined as good performing probiotic microorganisms. In fact, while the majority of probiotic lactobacilli are highly specialized for growth in a limited number of conditions. *L. plantarum* is able to colonize a wide range of environmental niches for its high metabolic versatility.

Among genes involved in biofilm development, *flmA*, *flmB*, and *flmC* have been identified in the *L. plantarum* LM3 strain, coding respectively for the proteins named FlmA, FlmB, and FlmC (1). The three protein show a high sequence homology with the LytR-CpsA-psr (LCP) domain. The LCP family gained attention upon the discovery that some members of this family influence various virulence factors as well as antibiotic resistance of important human pathogens. Particularly, in Gram-positive bacteria, LCP proteins are responsible for ligating cell wall teichoic acids to peptidoglycan (2). Here, in order to gain insight into the structure and the function of this interesting domain, we report the functional and structural characterization of the FlmC protein.

References: 1. Muscariello, L.; Marino, C.; Capri, U.; Vastano, V.; Marasco, R.; Sacco, M., CcpA and three newly identified proteins are involved in biofilm development in Lactobacillus plantarum. J Basic Microbiol 2013, 53 (1), 62-71. 2. Kawai, Y.; Marles-Wright, J.; Cleverley, R. M.; Emmins, R.; Ishikawa, S.; Kuwano, M.; Heinz, N.; Bui, N. K.; Hoyland, C. N.; Ogasawara, N.; Lewis, R. J.; Vollmer, W.; Daniel, R. A.; Errington, J., A widespread family of bacterial cell wall assembly proteins. EMBO J 2011, 30 (24), 4931-41.

Metal ion replacement by Pb(II), Ni(II) and Hg(II) in the prokaryotic zinc-finger domain

Valeria Sivo[a], *Gaetano Malgieri*[a], *Luigi Russo*[a], *Gianluca D'Abrosca*[a], *Rosa Iacovino*[a], *Anna Messere*[a], *Ilaria Baglivo*[a], *Paolo Vincenzo Pedone*[a], *Roberto Fattorusso*[a] *and Carla Isernia*[a].

[a] *Department of Environmental, Biological and Pharmaceutical Science and Technology, II University of Naples, via Vivaldi 43, 81100 Caserta, Italy; valeria.sivo@unicampania.it*

Zinc ion binding to the proteic domain is a principal event in the achievement of the correct fold in the classical zinc fingers domain since the motif is mainly unfolded in the absence of the metal cofactor. However, in the case of prokaryotic zinc finger the bigger ββββαα domain shows a hydrophobic core larger than the one found in eukaryotic zinc fingers and that plays a more relevant role in the folding mechanism. For these reasons, as great attention has been devoted to unveil the effect of metal ion replacement in zinc fingers and in zinc-containing proteins in general, the prokaryotic zinc finger domain appears to be a good model to study the interaction of exogenous metal ions with metallo-proteins.
We here explore the structural and functional consequences of the native Zn(II) substitution by Ni(II), Pb(II) and Hg(II) in Ros87, the DNA binding domain of the prokaryotic zinc finger protein Ros. Our findings will complement and extend previous results obtained for different eukaryotic zinc fingers, contributing to the evaluation of whether metal substitution in zinc fingers may be a relevant mechanism in the toxic and/or carcinogenic effects of metal ions.

References: 1. Chou, A. Y.; Archdeacon, J.; Kado, C. I., Proc Natl Acad Sci U S A 1998, 95 (9), 5293-8. 2. Malgieri, G.; Russo, L.; Esposito, S.; Baglivo, I.; Zaccaro, L.; Pedone, E. M.; Di Blasio, B.; Isernia, C.; Pedone, P. V.; Fattorusso, R., Proc Natl Acad Sci U S A 2007, 104 (44), 17341-6. 3. Baglivo, I.; Russo, L.; Esposito, S.; Malgieri, G.; Renda, M.; Salluzzo, A.; Di Blasio, B.; Isernia, C.; Fattorusso, R.; Pedone, P. V., Proc Natl Acad Sci U S A 2009, 106 (17), 6933-8.

Effect of vortex on the chirality induced in porphyrins assemblies by aminoacids

Rosalba Randazzo[a], *Massimiliano Gaeta*[a], *Luisa D'Urso*[a], *M. Elena Fragalà*[a], *Alessandro D'Urso*[a] *and Roberto Purrello*[a].

[a]*Università degli Studi di Catania V.le A. Doria 6, 95125 Catania; rrandazzo@unict.it*

There is great interest in the chirality transfer from the molecular scale to the supra-molecular non-covalent self-assembly level.(1)
Supramolecular chirality can derive from the complex nonsymmetric arrangement of various molecular components in a noncovalent ensemble. Even symmetric molecules, may present supramolecular chirality (i) by forming intrinsically chiral assemblies, or (ii) by aggregating on to chiral polymeric templates (extrinsic chirality).(2)
Moreover vortexes are a recognized example of macroscopic chirality and one possible origin of chiral symmetry-breaking in nature,(3) the relationship between vortexes and chirality of large assemblies is a very intriguing problem which might lead to understanding fundamentals of nature and, from this, to possible technological applications.(4,5)
Porphyrins are excellent building blocks to assemble supramolecular architectures. Their remarkable and tunable spectroscopic properties have been, in fact, exploited to design and realize a paramount number of porphyrin arrays potentially useful as sensors, optoelectronic devices, antenna systems, models of metallo enzymes, etc.
The tetra-anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) is not chiral, however in the opportune conditions of pH and ionic strength self-aggregation of its protonated (zwitterionic) form induces a split Circular Dichroism (CD) signal in the absorption region. Both positive (P) and negative (M) couplets are observed randomly. However the interaction between porphyrin and a chiral inducer allow obtaining a desired organization.
The capability of aminoacids to induce supramolecular chirality in the aggregated form of the protonate TPPS was investigated.
Being aware that vortexes (obtained by mechanical stirring) play a crucial role in the selection of equilibrium structures in porphyrins aggregates solutions, and that they can have two possible effects on supramolecular chirality, both static or dynamic (3,6-10) the effect of the mechanical stirring on the obtained systems was also studied.

References: 1. J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, **1995** VCH, Weinheim,. 2. R. Lauceri, A. D'Urso, A. Mammana, R. Purrello *Chirality* **2008** 20, 411–419. 3. A. Tsuda, M. A. Alam, T. Harada, T. Yamaguchi, N Ishii, T. Aida *Angew. Chem*. **2007**, 119, 8346 –8350. 4. A. D'Urso, R. Randazzo, L. Lo Faro, R. Purrello *Angew. Chem. Int. Ed.* **2010**, 49, 108 –112. 5. A. Di Mauro, R. Randazzo, S. F. Spano`, G. Compagnini, M. Gaeta, L. D'Urso, R. Paolesse, G. Pomarico, C. Di Natale, V. Villari, N. Micali, M. E. Fragala`, A. D'Urso, R. Purrello *Chem. Commun*., **2016**, 52, 13094—13096. 6. D. K. Kondepudi, R. J. Kaufman, N. Singh, Science 250 (1996) 975 – 976. 7. J. M. Rib, J. Crusats, F. Sague, J. Claret, R. Rubires, Science 292 (2001) 2063 – 2066. 8. W. Dzwolak, A. Loksztejn, A. Galinka-Rakoczj, R. Adachi, Y. Goto, L. Rupnicki, J. Am. Chem. Soc. 129 (2007) 7517 – 7522. 9.O. Ohno, Y. Kaizu, H. Kobayashi, J. Chem. Phys. 99 (1993) 4128 – 4139. e) T. Yamaguchi, T. Kimura, H. Matsuda, T. Aida, Angew. Chem. Int. Ed. 2004 43 (2004) 6350 – 6355. 10.M. Wolffs, S. J. George, Zˇ . Tomovic´, S. C. J. Meskers, A. P. H. J. Schenning, E. W. Meijer, Angew. Chem. Int. Ed. 46 (2007) 8203 – 8205.

Lipid synthesis model for lipid disruptors assessment using microsomal fraction of Mytilus galloprovincialis:

Analysis by High-Resolution Mass Spectrometry

Piergiorgio Cianciullo, Cesare Guercia and Cinta Porte.

Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain; e-mail: pgcqam@cid.csic.es

There is great interest in the chirality transfer from the molecular scale to the supra-molecular non-covalent self-assembly level.(1)
Supramolecular chirality can derive from the complex nonsymmetric arrangement of various molecular components in a noncovalent ensemble. Even symmetric molecules, may present supramolecular chirality (i) by forming intrinsically chiral assemblies, or (ii) by aggregating on to chiral polymeric templates (extrinsic chirality).(2)
Moreover vortexes are a recognized example of macroscopic chirality and one possible origin of chiral symmetry-breaking in nature,(3) the relationship between vortexes and chirality of large assemblies is a very intriguing problem which might lead to understanding fundamentals of nature and, from this, to possible technological applications.(4,5)
Porphyrins are excellent building blocks to assemble supramolecular architectures. Their remarkable and tunable spectroscopic properties have been, in fact, exploited to design and realize a paramount number of porphyrin arrays potentially useful as sensors, optoelectronic devices, antenna systems, models of metallo enzymes, etc.
The tetra-anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) is not chiral, however in the opportune conditions of pH and ionic strength self-aggregation of its protonated (zwitterionic) form induces a split Circular Dichroism (CD) signal in the absorption region. Both positive (P) and negative (M) couplets are observed randomly. However the interaction between porphyrin and a chiral inducer allow obtaining a desired organization.
The capability of aminoacids to induce supramolecular chirality in the aggregated form of the protonate TPPS was investigated.
Being aware that vortexes (obtained by mechanical stirring) play a crucial role in the selection of equilibrium structures in porphyrins aggregates solutions, and that they can have two possible effects on supramolecular chirality, both static or dynamic (3,6-10) the effect of the mechanical stirring on the obtained systems was also studied.

References: 1. J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, **1995** VCH, Weinheim,. 2. R. Lauceri, A. D'Urso, A. Mammana, R. Purrello *Chirality* **2008** 20, 411–419. 3. A. Tsuda, M. A. Alam, T. Harada, T. Yamaguchi, N Ishii, T. Aida *Angew. Chem*. **2007**, 119, 8346 –8350. 4. A. D'Urso, R. Randazzo, L. Lo Faro, R. Purrello *Angew. Chem. Int. Ed.* **2010**, 49, 108 –112. 5. A. Di Mauro, R. Randazzo, S. F. Spano`, G. Compagnini, M. Gaeta, L. D'Urso, R. Paolesse, G. Pomarico, C. Di Natale, V. Villari, N. Micali, M. E. Fragala`, A. D'Urso, R. Purrello *Chem. Commun*., **2016**, 52, 13094—13096. 6. D. K. Kondepudi, R. J. Kaufman, N. Singh, Science 250 (1996) 975 – 976. 7. J. M. Rib, J. Crusats, F. Sague, J. Claret, R. Rubires, Science 292 (2001) 2063 – 2066. 8. W. Dzwolak, A. Loksztejn, A. Galinka-Rakoczj, R. Adachi, Y. Goto, L. Rupnicki, J. Am. Chem. Soc. 129 (2007) 7517 – 7522. 9.O. Ohno, Y. Kaizu, H. Kobayashi, J. Chem. Phys. 99 (1993) 4128 – 4139. e) T. Yamaguchi, T. Kimura, H. Matsuda, T. Aida, Angew. Chem. Int. Ed. 2004 43 (2004) 6350 – 6355. 10.M. Wolffs, S. J. George, Zˇ . Tomovic´, S. C. J. Meskers, A. P. H. J. Schenning, E. W. Meijer, Angew. Chem. Int. Ed. 46 (2007) 8203 – 8205.

Peptide Nucleic Acid dimers self assemble into highly fluorescent aggregates

Concetta Avitabile[a] , Antonella Accardo,[b], Flavia Mercurio[a], Marilisa Leone[a], Bartolomeo della Ventura[c], Michele Saviano[d], Raffaele Velotta[c], Giancarlo Morelli[b], Alessandra Romanelli[b].

[a] Istituto di Biostrutture e Bioimmagini, CNR, via Mezzocannone 16, 80134 Napoli; [b]Dipartimento di Farmacia, Università di Napoli "Federico II", via Mezzocannone 16, 80134 Napoli; [c]Dipartimento di Fisica, Università di Napoli "Federico II", via Cinthia 26, 80126 Napoli; Istituto di Cristallografia, CNR, via Giovanni Amendola, 122/O, 70126 Bari.

The self-assembly of nucleobases has been extensively investigated with the aim to produce new materials, electronic nanodevices and biosensors (1). Interactions between nucleobases occur not only by Watson-Crick or Hoogsteen hydrogen bonding, as observed in the DNA double and triple helices; many base pairing motifs between the four standard nucleobases characterized by two hydrogen bonds have been identified and these are at the base of self-assembling processes. In solution 5' guanine monophosphate (5' GMP) forms g quartets which are stabilized by cations such as Na+ and K+, where each cation interacts with two stacked quartets. At high 5'-GMP concentrations (18-34 wt%) 27 to 87stacked quartets generate 8-30 nm cylinders, kept together exclusively by hydrogen bonding, □-□ stacking and cation-dipole interactions (2). Self-assembly of cytosine, thymine, adenine and uracil has been explored mostly on solid surfaces, such as on Au or on Cu surfaces (3), revealing the formation of 1D and 2D supramolecular nanostructures. The assembly of nucleobases in the context of Peptide Nucleic Acids (PNA) is so far very little investigated. Recently Gazit et la. described the ability of PNA dimers to self assemble into organized structures, guided by stacking interactions and Watson-Crick base pairing (4). GC dimers exhibit interesting fluorescent and optoelectronic properties, showing promise for application as organic light emitting diodes. Encouraged by these interesting results, we initiated our investigation on the self-assembly of Peptide Nucleic Acids, focusing on the PNA dimer Fmoc-GC. Introduction of the fluorenylmethoxy carbonyl (Fmoc) moiety was hypothesized to affect the aggregation properties and likely also the optical properties of the PNA dimer. We here report the characterization of the optical and structural properties of the aggregates by fluorescence, Nuclear Magnetic Resonance and Dynamic Light Scattering. Aggregation of Fmoc GC is mediated by Watson-Crick hydrogen bonds and results in highly fluorescent compounds.

References: 1. Davis, J. T. and G. P. Spada (2007) Chemical Society reviews 36(2): 296-313. 2. Wong, A., R. Ida, et al. (2005) Journal of the American Chemical Society 127(19): 6990-6998. 3. Liu, L., D. Xia, et al. (2014) International journal of molecular sciences 15(2): 1901-1914. 4. Berger, O., L. Adler-Abramovich, et al. (2015) Nature Nanotechnology 10(4): 353-360.

Molecular characterization in solution of a bis-histidine-peptide complexed to Re(I)-tricarbonyl

Luca D. D'Andrea[a] Gaetano De Tommaso[b], Veronica Celentano[a], Lucia De Rosa[a], Alessandra Romanelli[c], Gaetano Malgieri[d], Mauro Iuliano[b], Carla Isernia[d].

[a] Istituto di Biostrutture e Bioimmagini, CNR, Napoli, Italy; [b] Dipartimento di Scienze Chimiche, Università di Napoli "Federico II", Napoli, Italy; [c] Dipartimento di Farmacia, Università di Napoli "Federico II", Napoli, Italy; [d] Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Università della Campania "L. Vanvitelli", Caserta, Italy; carla.isernia@unicampania.it

Radiolabeled peptides are useful in the diagnosis and therapy of a variety of human disease characterized by overexpression of peptide receptors. They present some advantages such as: high binding affinity and specificity for the cognate receptor, they are easily synthesized and modified and have rapid blood clearance. These molecules are usually composed by the targeting molecule, a linker and a bifunctional ligand which binds to the radioactive metal. Several radiometals are being used in nuclear medicine and ^{99m}Tc(I) is rapidly gaining in popularity since the introduction of mild synthetic procedure to prepare stable Tc(I)- or Re(I)-complexes $[Tc(H_2O)_3(CO)_3]$ (TcCO) or $[Re(H_2O)_3(CO)_3]$ (ReCO). In these complexes the water molecules can be replaced by ligands to obtain d6 low spin complexes. Ligands replacing all water molecules can form very stable complexes, avoiding trans-chelation reactions which may occur in vivo and the generation of free metal. Histidine is considered a good ligand for TcCO/ReCO and when positioned at the N-terminus of a peptide it acts as bidentate ligand. We reported the *in vitro* and *in vivo* characterization of the peptide CCK8 decorated with a histidine based chelator labeled with ^{99m}Tc-tricarbonyl (1). Recently, we reported the speciation, affinity and binding features of histidine and imidazole complexed to ReCO. In the present work, we analyze the solution properties of the histidine-based chelator complexed to ReCO by NMR and other spectroscopic techniques in order to highlight the molecular properties in aqueous solution of the peptide-metal complex.

References: 1. D'Andrea LD, Testa I, Panico M, Di Stasi R, Caracò C, Tarallo L, Arra C, Barbieri A, Romanelli A, Aloj L In vivo and in vitro characterization of CCK8 bearing a histidine-based chelator labeled with 99mTc-tricarbonyl Biopolymers 2008, 90, 707-712. 2. De Tommaso G, Celentano V, Malgieri G, Fattorusso R, Romanelli A, D'Andrea LD, Iuliano M, Isernia C fac-[Re(H2O)3(CO)3]+ Complexed with Histidine and Imidazole in aqueous solution: Speciation, Affinity and Binding Features ChemistrySelect 2016, 1, 3739-3744.

Chemical synthesis of all-D Axl domains for mirror image phage display

Lucia De Rosa[a], *Rossella Di Stasi*[a] *and Luca D. D'Andrea*[a].

[a] *Istituto di Biostrutture e Bioimmagini, CNR, Napoli, Italy; luca.dandrea@cnr.it*

Axl is a tyrosine kinases receptor belonging to the TAM family, which also includes Tyro-3 and Mer members. Axl signaling plays important role in several cellular responses, as the receptor activation promotes cellular proliferation, survival, adhesion, migration, autophagy, invasion, angiogenesis, platelet aggregation and natural killer cells differentiation. Besides, Axl is potent negative regulator of innate immune responses, thus protecting against an overzealous inflammatory response. Structurally, Axl is characterized by an extracellular domain containing two N-terminal immunoglobulin (Ig)-like domains and two fibronectin type III (FNIII) repeats, a transmembrane domain and a cytoplasmic tyrosine kinase domain. Axl can be activated through a number of different mechanisms, mainly upon ligand-induced dimerization. The vitamin K-dependent growth arrest-specific 6 (Gas6) protein is the principal natural ligand of Axl receptor. The C-terminal region of Gas6 comprising LG domains is sufficient for Axl receptor binding and activation. Only the LG region of Gas6 interacts with Ig-like domains of Axl receptor. Upon binding of Gas6 to Axl Ig-like domains, the receptor dimerizes and its tyrosine kinase domain becomes activated.
We intend develop Axl peptide for therapeutic application using the approach called "mirror phage display library". To get this aim we need to prepare the Axl interacting domains Ig1 and Ig2 with all D-amino acids. The D-protein will be immobilized on a solid support and used as bait to find binders through phage display library screening. The selected L-peptide binds to the all-D protein, this implies that the D-peptide will bind the natural L-protein. In this way a metabolically stable D-peptide binder will be developed. Here, we report the chemical strategy to prepare the all-D Axl domain by native chemical ligation.

Conformational stabilization of a β-hairpin peptide through a triazole-trpyptophan interaction

Donatella Diana [a], Veronica Celentano [a], Lucia De Rosa [a], Alessandra Romanelli [b], Roberto Fattorusso [c], Luca D. D'Andrea [a].

[a] Istituto di Biostrutture e Bioimmagini, CNR, Napoli, Italy; [b] Dipartimento di Farmacia, Università di Napoli "Federico II", Napoli, Italy; [c] Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Università della Campania "L. Vanvitelli", Caserta, Italy; roberto.fattorusso@unicampania.it

β-hairpin peptides are useful molecules for pharmaceutical and biotechnological applications. They are especially attractive to modulate protein-protein interactions. Stability and formation of β-hairpin have been deeply analyzed and molecular tools have been developed to design conformational stable β-hairpin peptides. Recently, we have analyzed the conformational stability of a series of β-hairpin peptides presenting a triazole bridge, with variable lengths, in a non-hydrogen bonded position (NHB) (1) and in a hydrogen-bonded position (HB) (2). The "triazole bridge" is a 1-4 disubstituted 1,2,3 triazole obtained by side chain-side chain cyclization through Cu-catalyzed alkyne-azide cycloaddition (CuAAC) forming a covalent linkage between the two strands. In these previous works we have established that the formation of the intrastrand triazole bridge is an effective strategy to constrain peptides in a stable β-hairpin conformation and the optimal bridge length depends on the specific β-hairpin position (NHB or HB) of the tool.
In this work, we wish to obtain a conformational stable β-hairpin peptide combining aromatic interactions with an interstrand covalent linkage such as the triazole bridge. To get this aim we designed a series of β-hairpin peptides presenting the triazole bridge in a diagonal non hydrogen bond (DNHB) position close to the side chains of a tryptophan. Peptides were analyzed by NMR spectroscopy to evaluate their β-hairpin content

References: 1. Celentano V, Diana D, De Rosa L, Romanelli A, Fattorusso R, D'Andrea LD. β-Hairpin stabilization through an interstrand triazole bridge. Chem Commun. 2012, 48, 762-764. 2. Celentano V, Diana D, Di Salvo C, De Rosa L, Romanelli A, Fattorusso R, D'Andrea LD. 1,2,3-Triazole Bridge as Conformational Constrain in β-Hairpin Peptides: Analysis of Hydrogen-Bonded Positions. Chemistry. 2016, 22, 5534-5537.

Enzymatic Ubiquitination of Tau protein

Carlo Giorgio Barracchia[a], *Francesca Munari*[a], *Giorgio Arrigoni*[c], *Michael Assfalg*[a], *Andrea Bortot*[a], *Stefano Capaldi*[b], *Serena Zanzoni*[a], *Mariapina D'Onofrio*[a].

[a] *Biomolecular NMR Laboratory and* [b] *Biocrystallography Laboratory, Department of Biotechnology, University of Verona, Ca' Vignal 1, Strada Le Grazie 15, 37134 Verona, Italy;* [c] *University of Padua, Department of Biomedical Science, Padova, Italy; carlogiorgio.barracchia@univr.it*

The deposition of protein Tau in intracellular neurofibrillary tangles is a major hallmark of Alzheimer's disease (AD) and other tauopathies. Tau is a microtubule associated protein that modulates the stability of axonal microtubules. A large variety of post-translational modifications were found in Tau, including phosphorylation, glycosylation, acetylation, truncation, ubiquitination and prolyl-isomerization (1, 2). Recent evidence indicated that, besides phosphorylation, polyubiquitin also marks Tau in paired helical filaments purified from AD brains (3). Polyubiquitination regulates fundamental cellular pathways, including protein turnover by proteasomal degradation. Due to its role in the clearance of misfolded proteins, dysfunction of the ubiquitin-proteasome system was proposed to be one of the key mechanisms of neurodegeneration. Indeed, a failure of proteasome function may cause the accumulation of ubiquitinated proteins such as Tau, exacerbating aggregation and neurotoxicity. In this context, we aim to define the effect of polyubiquitination on the structural propensities of Tau, on its aggregation pathway to fibrils, and on its clearance. The implementation of this research requires the obtainment of high amounts of Tau modified at specific lysine residues with polyubiquitin chains. We are currently focusing our attention on a enzymatic method. Ubiquitination of substrates is catalyzed in vivo by three enzymes: ubiquitin-activating (E1s), ubiquitin-conjugating (E2s), and ubiquitin ligase (E3s). Substrate specificity is given by recognition of the target protein by E3. CHIP, an E3 enzyme which targets misfolded proteins towards proteasomal degradation, can ubiquitinate Tau in vitro in combination with Ubch5 (an E2) and E1 enzymes (4). We tried to use Ubc13, an alternative E2 enzyme that was shown to interact with CHIP (5). Our preliminary results show that both combinations of E1-Ubch5b-CHIP, and E1-Ubc13-CHIP can ubiquitinate Tau. In order to determine the ubiquitination sites on Tau, we plan to perform mass spectrometry analysis. The work is in progress to control the enzymatic reaction in order to obtain homogenously modified samples, and to extend the polyubiquitin chain.

References: 1. Spillantini, M. G. and Goedert, M. *Lancet Neurol.* 2013, *12*, 609-22. 2. Latypova, X.; and Terro, F. *Neurochem Int.* 2011, *58*, 458-71. 3. Cripps, D.; Thomas, S. N.; Jeng, Y. et al. *J Biol Chem.* 2006, *281*, 10825-38. 4. Petrucelli, L. et al. *Hum Mol Genet.* 2004, *13*, 703-14;]. 5. Zhang, M. et al. *Mol Cell.* 2005, *20*, 525-38.

Selective $\alpha_v\beta_3$-targeting theranostic in malignant melanoma: design, synthesis and biological studies of a new RGD peptide

Daniela Comegna[a], Antonella Zannetti[b], Annarita Del Gatto[a,c], Ivan de Paola[a], Sonia Di Gaetano[a,c], Annamaria Liguoro[a], Domenica Capasso[d], Michele Saviano[c,e], Laura Zaccaro[a,c]

[a]Institute of Biostructures and Bioimaging-CNR, Via Mezzocannone 16, 80134, Naples, Italy; [b]Institute of Biostructures and Bioimaging-CNR, Via De Amicis 95, 80145 Naples, Italy; [c]Interdepartmental Center of Bioactive Peptide, University of Naples ''Federico II'', Via Mezzocannone 16, 80134 Naples, Italy; [d]Department of Pharmacy, University of Naples ''Federico II'', Via Mezzocannone 16, 80134 Naples, Italy; [e]Institute of Crystallography-CNR, Via Amendola 122/O, 70126 Bari, Italy;
lzaccaro@unina.it

Malignant melanoma is the most aggressive form of skin cancer having strong tendency to metastasize and it is responsible for 80% of all deaths caused by tumors affecting this tissue (1). Also, melanoma is resistant to most treatment regimens such as chemotherapy and immunotherapy (2). The key objective to improve melanoma pharmacological therapy lies in the ability to early visualize and inhibit the dissemination of cancer cells that eventually contribute to the onset of secondary tumor sites. It is well documented that in melanoma high expression of $\alpha_v\beta_3$ integrin is correlated with tumor invasion and poor prognosis (3). Here we reported the design, synthesis and biological characterization of the novel peptide Ψ-RGDechi, selective for $\alpha_v\beta_3$ integrin, as theranostic agent in malignant melanoma. Respect to the parental peptide RGDechi (4,5,6,7), Ψ-RGDechi shows high resistance to proteases. Its ability to selectively inhibit cell adhesion, migration and invasion, key steps highly related in the metastatic cascade, was demonstrated in a human metastatic melanoma cell line highly expressing $\alpha_v\beta_3$ integrin. Also, labelled Ψ-RGDechi peptide was able to selectively detect human melanoma xenografts by near-infrared fluorescence.

References: 1. MacKie, R. M., Hauschild, A. & Eggermont, A. M. Epidemiology of invasive cutaneous melanoma. *Ann Oncol* 20 Suppl 6, vi1-7, doi:10.1093/annonc/mdp252 (2009). 2. Arozarena, I. & Wellbrock, C. Targeting invasive properties of melanoma cells. *Febs J*, doi:10.1111/febs.14040 (2017). 3. Bendas, G. & Borsig, L. Cancer cell adhesion and metastasis: selectins, integrins, and the inhibitory potential of heparins. *Int J Cell Biol* 2012, 676731, doi:10.1155/2012/676731 (2012). 4. Del Gatto, A. *et al.* Novel and selective alpha(v)beta3 receptor peptide antagonist: design, synthesis, and biological behavior. *J Med Chem* 49, 3416-3420, doi:10.1021/jm060233m (2006). 5. Zannetti, A. *et al.* Imaging of alpha(v)beta(3) expression by a bifunctional chimeric RGD peptide not cross-reacting with alpha(v)beta(5). *Clin Cancer Res* 15, 5224-5233, doi:10.1158/1078-0432.CCR-08-3270 (2009). 6. Santulli, G. *et al.* Evaluation of the anti-angiogenic properties of the new selective alphaVbeta3 integrin antagonist RGDechiHCit. *J Transl Med* 9, 7, doi:10.1186/1479-5876-9-7 (2011). 7. Pisano, M. *et al.* In vitro activity of the alphavbeta3 integrin antagonist RGDechi-hCit on malignant melanoma cells. *Anticancer Res* 33, 871-879 (2013).

Elenco degli Autori

*Autore presentatore

Velotta Raffaele	CSB PO15
Zaccaro Laura*	CSB PO20
Zannetti Antonella	CSB PO20
Zanzoni Serena	CSB OR10
	CSB PO19
Ziche Marina	CSB PO02
Zimbone Stefania	CSB OR09

DIVISIONE DI SPETTROMETRIA DI MASSA

Comitato Scientifico

- Donatella Caruso, Università degli Studi di Milano
- Giorgio G. Mellerio, Università degli Studi di Pavia
- Gianluca Giorgi, Università degli Studi di Siena
- Gianluca Bartolucci, Università degli Studi di Firenze
- Giuliana Bianco, Università degli Studi della Basilicata
- Roberta Galarini, Istituto Zooprofilattico Sperimentale Umbria e Marche
- Michele Suman, Barilla G.R. F.lli S.p.A.
- Cecilia Bergamini, Arpae Emilia Romagna
- Emanuela Gregori, Istituto superiore di Sanità, Roma
- Fulvio Magni, Università di Milano Bicocca
- Luisa Mattoli, Aboca S.p.A.
- Federico Riccardi Sirtori, Nerviano Medical Science
- Alessandro Buchicchio, Università degli Studi della Basilicata
- Federica Camin, Fondazione E. Mach

Delegato di Divisione

- Paola Montoro, Università degli Studi di Salerno

Programma Scientifico

Divisione Spettrometria di Massa

Lunedì 11 Settembre 2017

	Sala Cassandra
Sessione Metabolomica e Lipidomica	
Chairperson: Donatella Caruso	
9:00 – 9:30	*Apertura lavori divisione*
9:30-10:10	MAS PL01: Nico Mitro, Matteo Audano, Silvia Pedretti, Maurizio Crestani, Enrique Saez, Emma De Fabiani and Donatella Caruso *Metabolomic approaches to unravel the role of a novel mitochondrial regulator*
10:10-10:30	MAS OR01: Laura Goracci, Sara Tortorella, Paolo Tiberi, Roberto Maria Pellegrino, Alessandra Di Veroli, Aurora Valeri, Lucia Cesarini, Gabriele Cruciani *Lipostar, a novel platform-neutral cheminformatics tool for untargeted and targeted lipidomics*
10:30 – 11:00	Coffee Break
Sessione Metabolomica e Lipidomica	
Chairperson: Donatella Caruso	
11:00 – 11:20	MAS OR02: Gianluca Giorgi *Metabolic fingerprinting of plants and wines*
11:20 – 11:40	MAS OR03: Simona Scarpella, Arthur Moseley, Chris Hughes, Erik J. Soderblom, Keith Richardson, Will Thompson, Johannes PC Vissers, Jason Wildgoose, James Langridge *Qualitative and quantitative characterization of a novel DIA method for omics analysis*
11:40 – 12:00	MAS OR04: Calogera Monastero, Antonella Maggio, Antonio Mazzola, Santino Orecchio, Marco Torri, Bernardo Patti, Angela Cuttitta *Qualitative and quantitative analysis of fatty acids extracted from pelagic species of the Sicilian Channel, comparison with endogenous variables*
12:00 – 12:20	MAS OR05: Gilda D'Urso, Cosimo Pizza, Sonia Piacente, Paola Montoro *LC-MS based metabolomics and evaluation of the antioxidant activity of Fragaria vesca leaves*
12:20 – 12:40	MAS OR06: Luisa Mattoli, Cangi Francesca, Burico Michela, Anna Gaetano, Lorenzo Tafini, Fodaroni Giada, Stella Bedont, Sara Tamimi, Denise De Carli, Simona Propersi, Veronica Ercolani, Valentina Fiordelli, Enrico Flamini, Luca Grigi *Mass Spectrometry and natural complex products metabolomic analysis*
12:40 – 13:00	MAS OR07: Mariateresa Maldini *-OMICS world: take it easy! Solutions to Advance your Metabolomics Research*
13:00 – 14:00	Intervallo Pranzo

	Sala Cassandra
Sessione Congiunta Chimica Analitica Spettrometria di Massa	
Chairperson: Tommaso Cataldi	
15:00 – 15:30	ANA/MAS KN01: Cosima Damiana Calvano, Marco Glaciale, Sara Granafei, Anna Maria Sardanelli, Luana Bellanova, Antonella Mastrorocco, Francesco Palmisano, Tommaso R.I Cataldi *Advanced mass spectrometric techniques for the untargeted lipidome characterization of fibroblasts in early on-set Parkinson's disease patients*
15:30 – 15:50	ANA/MAS OR01: Simone Nicolardi, Yuri E.M. van der Burgt, Jeroen D.C. Codée, Manfred Wuhrer, Cornelis, H. Hokke, Fabrizio Chiodo *Structural characterization of bio-functionalized gold nanoparticles by ultrahigh resolution mass spectrometry.*

15:50 – 16:10	ANA/MAS OR02: Lucia Cenci, Graziano Guella, Alessandra Maria Bossi *Molecularly imprinted materials coupled to MALDI-TOF Mass Spectrometry for the targeted analysis of peptides and proteins.*
16:10 – 16:30	ANA/MAS OR03: Rossana Scarpone, Roberta Rosato, Federico Bacá, Manuel Sergi, Dario Compagnone *Unknown and non-target analysis to determine pesticides in fruit and vegetables by means of UHPLC-HRMS (Orbitrap)*
16:30 – 17:00	Coffee Break
Sessione Congiunta Chimica Analitica Spettrometria di Massa	
Chairperson: Paola Montoro	
17:00 – 17:30	ANA/MAS KN02: Danilo Sciarrone, Antonino Schepis, Luigi Mondello *Advanced analytical capabilities exploiting isotope ratio mass spectrometry and quadrupole mass spectrometry coupled to multidimensional gas chromatography*
17:30 – 17:50	ANA/MAS OR04: Andreina Ricci, Paola Cimino, Anna Troiani, Federico Pepi, Stefania Garzoli, Chiara Salvitti and Vincenzo Barone *From ascorbic acid to furan molecules: a theoretical and experimental study on the gas phase acid catalyzed degradation of vitamin C*
17:50 – 18:10	ANA/MAS OR05: Veronica Termopoli, Pierangela Palma, Giorgio Famiglini, Maurizio Piergiovanni, Achille Cappiello *Liquid-EI (LEI) Atmospheric Pressure Mechanism for the introduction of liquid streams into an unmodified electron ionization source of a mass spectrometer.*
18:10 – 18:30	ANA/MAS OR06: Chiara Salvitti, Andreina Ricci, Federico Pepi, Stefania Garzoli, Anna Troiani, Giulia De Petris, Marzio Rosi *Selective gas-phase conversion of D-fructose to 5-hydroxymethylfuraldehyde through a base-assisted dehydration process*

Martedì 12 Settembre 2017

	Sala Cassandra
Sessione Isotopi stabili	
Chairperson: Gianluca Giorgi	
9:00 – 9:40	MAS PL02: Federica Camin, Matteo Perini, Luana Bontempo *Stable isotope ratios for food authentication and traceability*
9:40 – 10:00	MAS OR08: Antonella Macrì, Paola Iacumin *Stable isotopes in fossil remains and environmental reconstruction*
10:00 – 10:20	MAS OR09: Alessandro Pratesi, Tiziano Marzo, Damiano Cirri, Luigi Messori *Mass spectrometry and metallomics: a powerful technique to delineate the mode-of-action of anticancer metallodrugs. The case of Oxaliplatin and its analogues*
10:20 – 10:40	MAS OR10: Lionnel Mounier, Luca Simonotti, Andreas Hilkert *Chromatography-based EA-IRMS: redesigning the elemental analyzer around modern chromatographic principles to match the challenges of today's and tomorrow's applications*
10:40 – 11:00	Coffee Break
Sessione Life Sciences	
Chairperson: Nico Mitro	
11:00 – 11:40	MAS PL03: Violette Gautier, Linsey Raaijmakers, Christian K. Frese, Renske Penning, Charlotte A.G.H. van Gelder, Thierry Schmidlin, Gianluca Maddalo, Kristel Kemper, Oscar Krijgsman, Marina Mikhaylova, Riccardo Stucchi, Qingyang Liu, Harm Post, Markus Brockmann, Vincent A. Blomen, Joppe Nieuwenhuis, Elmer Stickel, Matthijs Raaben, Onno B. Bleijerveld, Lucas T. Jae, Thijn R. Brummelkamp, Shabaz Mohammed, Albert J. R. Heck, Casper C. Hoogenraad, Daniel S. Peeper and A.F. Maarten Altelaar *High-resolution proteomics, integrative phosphoproteomics and targeted mass spectrometry to unravel complex biology*

11:40 – 12:00	MAS OR11: Maurizio Piergiovanni, Achille Cappiello, Giorgio Famiglini, Veronica Termopoli, Pierangela Palma *Determination of benzodiazepines in beverages using green extraction methods and HPLC-UV detection*
12:00 – 12:20	MAS OR12: Marcello Manfredi, Eleonora Conte, Elisa Robotti, Elettra Barberis, Fabio Gosetti, Eleonora Mazzucco, Valeria Caneparo, Ester Vanni, Santo Landolfo, Marisa Gariglio, Marco De Andrea, Emilio Marengo *Quantification of Plasma Proteins with micro-LC SWATH®-MS for Biomarker Discovery in Inflammatory Bowel Disease*
12:20 –12:40	MAS OR13: Ilaria Santoro, Giovanni Sindona, Monica Nardi, Cinzia Benincasa *Improvements of extraction and identification methodologies of PUFA from algae*
12:40 –13:00	MAS OR14: Roberto Spezzano, Gaia Cermenati, Mariateresa Maldini, Silvia Pedretti, Matteo Audano, Silvia Giatti, Marzia Pesaresi, Roberto Cosimo Melcangi, Nico Mitro, Donatella Caruso *Lack of sterol regulatory element binding protein-1c induces alteration of neuroactive steroid levels in sciatic nerve*

13:00 – 14:00	Intervallo Pranzo

	Sala Paestum B
14:00 – 15:00	*Sessione Poster 1 (MAS PO01 – MAS PO05)*

Conferenze Plenarie

- MAS PL01: Nico Mitro, Università degli Studi di Milano
- MAS PL02: Federica Camin, Fondazione Edmund Mach
- MAS PL03: A.F. Maarten Altelaar, Utrecht Institute for Pharmaceutical Sciences

Metabolomic Approaches to Unravel the Role of a Novel Mitochondrial Regulator

Nico Mitro[a], Matteo Audano[a], Silvia Pedretti[a], Maurizio Crestani[a], Enrique Saez[b], Emma De Fabiani[a] and Donatella Caruso[a]

[a]Dipartimento di Scienze Farmacologiche e Biomolecolari, Università degli Studi di Milano, Via Balzaretti 9, 20133, Milano, Italy. b The Skaggs Institute for Chemical Biology, The Scripps Research Institute, La Jolla, CA 92037, USA.

Metabolomics is a powerful tool to gain new insights contributing to the identification of complex molecular mechanisms in human and animal cells. Our aim was to identify novel factors regulating mitochondria with the final goal to gain further knowledge on the links between energy metabolism and key cell processes. We isolated Zinc Finger CCCH-Type Containing 10 (Zc3h10), a gene not yet linked to mitochondria, as a novel mitochondrial regulator. We found that Zc3h10 is essential for mitochondrial activity. However, its role in metabolism is still unknown. We performed transcriptomic analysis in proliferating myoblasts treated with scramble or shRNA against Zc3h10 to down-regulate Zc3h10 expression. Gene Set Enrichment Analysis (GSEA) of transcriptomic data revealed that Zc3h10 positively associated with mitochondria-related metabolic pathway (i.e. α-Ketoglutarate metabolic process). Next, we also evaluated proteomic profile in Zc3h10 knock-down myoblasts. This experiment identified a total of 3755 proteins of which 137 up- and 170 down-regulated by the silencing of Zc3h10. Gene Ontology (GO) analyses detected statistically enrichment of biological processes only for down-regulated proteins among which electron transport chain (ETC).

To gain further insights into metabolic phenotype driven by Zc3h10 knock-down in myoblasts, we used targeted metabolomic analysis. Steady-state metabolomics indicated that Zc3h10 silencing increased AMP and ADP and concomitantly decreased ATP and NADH levels. These latter data are in line with proteomic experiment showing reduced levels of some subunits of the ETC. Furthermore, we also observed reduced levels of pyruvate, α-ketoglutarate (α-KG), fumarate, malate and oxaloacetate (OAA) and increased levels of succinate. Next, we interrogated MetaboAnalyst 3.0 (1, 2) to integrate, independently, data from transcriptomic or proteomic profile with metabolomics. Both integrated analyses revealed that tricarboxylic acid (TCA) cycle is the most affected pathway.

Based on these evidences, to gain more detailed insights into mitochondrial substrate utilization we cultured myoblasts in the presence of [U-$^{13}C_6$]glucose or [U-$^{13}C_{16}$]palmitate or [U-$^{13}C_5$]glutamine. These analyses indicated that palmitate and glucose utilization, based on fully labeled and M2 acetyl-CoA levels, were not affected in Zc3h10 silenced cells. However, fully labeled glucose-derived α-KG and palmitate-derived fumarate and OAA were decreased relative to scramble controls. In addition, we observed higher levels of fully labeled glutamine-derived α-KG indicating increased anaplerosis. Isotopic enrichment was used to provide additional insight into TCA cycle activity. We observed reduced levels of glucose-derived M2 α-KG and M4 succinyl-CoA, of palmitate-derived M3 fumarate and M3 OAA suggesting a slower TCA cycle function in Zc3h10 depleted cells compared to scramble control. In addition, glutamine oxidative metabolism was also decreased as evidence from M4 malate and M4 citrate.

Taken together, these data demonstrate that Zc3h10 silencing primarily leads to altered ETC activity, which in turn, negatively impacts TCA cycle function.

Acknowledgements. Supported by the European Foundation for the Study of Diabetes (EFSD).

References: 1. Xia, J., Sinelnikov, I.V., Han, B., and Wishart, D.S. (2015). MetaboAnalyst 3.0--making metabolomics more meaningful. Nucleic Acids Res *43*, W251-257. 2. Xia, J., and Wishart, D.S. (2010). MetPA: a web-based metabolomics tool for pathway analysis and visualization. Bioinformatics *26*, 2342-2344.

Stable Isotope Ratios for Food Authentication and Traceability

Federica Camin[a], *Matteo Perini*[a], *Luana Bontempo*[a]

[a]Fondazione Edmund Mach, via Mach 1 38121 San Michele all'Adige (TN)
e-mail: Federica.camin@fmach.it

Determining the authenticity of foods means uncovering non-compliance with the established legislative standards, substitution with cheaper but similar ingredients, extension of food using adulterants, misdescription of origin (e.g. geographical), species or production method (e.g. organic vs conventional). Nowadays, the objective assessment of food authenticity is of paramount importance as consumers come into daily contact with a wide variety of foods. Traceability has thus become a cornerstone of the EU's food safety policy.

Methods for testing authenticity and providing analytical data on traceability require robust analytical techniques that can be utilised by the various regulatory authorities. Of the many techniques available, one of the most widely-used is isotope ratio mass spectrometry (IRMS), applied since around 1975 to detect adulteration of products like wine, honey, fruit juice, maple syrup, vinegar with cheaper extenders, such as sugar, or simply water. Those "traditional" applications of stable isotopes in food control rely on the analysis of the isotopic ratios of only one or two elements ($^{13}C/^{12}C$ and/or $^{18}O/^{16}O$, $^{13}C/^{12}C$ and $^{2}H/^{1}H$) and several of these methods have been officially validated and acknowledged as AOAC, CEN, EU or OIV methods. More recently multi-isotope ratio analysis ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{2}H/^{1}H$, $^{34}S/^{32}S$) sometimes combined with $^{87}Sr/^{86}Sr$ and elemental profiling and GC- or HPLC- IRMS, have been successfully applied for verifying geographical origin and organic production of food (e.g. cereal, tomato, meat, cheese) and for identifying the natural origin of flavours (e.g. vanillin) and bioactive molecules (e.g. Monacolin K).

High-Resolution Proteomics, Integrative Phosphoproteomics and Targeted Mass Spectrometry to Unravel Complex Biology

Violette Gautier[a], Linsey Raaijmakers[a], Christian K. Frese[a], Renske Penning[a], Charlotte A.G.H. van Gelder[a], Thierry Schmidlin[a], Gianluca Maddalo[a], Kristel Kemper[b], Oscar Krijgsman[b], Marina Mikhaylova[c], Riccardo Stucchi[c], Qingyang Liu[c], Harm Post[a], Markus Brockmann[b], Vincent A. Blomen[b], Joppe Nieuwenhuis[b], Elmer Stickel[b], Matthijs Raaben[b], Onno B. Bleijerveld[b], Lucas T. Jae[b], Thijn R. Brummelkamp[b], Shabaz Mohammed[a], Albert J. R. Heck[a], Casper C. Hoogenraad[c], Daniel S. Peeper[b] and A.F. Maarten Altelaar[a]

[a]*Biomolecular Mass Spectrometry and Proteomics, Utrecht Institute for Pharmaceutical Sciences, University of Utrecht, Padualaan 8, 3584CH Utrecht, The Netherlands,* [b]*Netherlands Cancer Institute, Plesmanlaan 121, 1066 CX, Amsterdam, The Netherlands.* [c]*Cell Biology, Department of Biology, Faculty of Science, Utrecht University, 3584 CH Utrecht, The Netherlands.*

Society is dealing with great challenges regarding the health of its population, reflected in the increase in incidences of diseases like cancer and neurological disorders. Many of these diseases have underlying DNA mutations; however, the molecular basis maintaining and expanding the disease can be found at the level of the cellular proteome. Here, expression, degradation, interactions, or localization determine protein function, and alteration in protein function can be associated with disease. The regulation of protein function is largely achieved by post-translational modifications (PTMs) on these proteins, which influence their behavior to a large extent. In particular protein phosphorylation is well known for its essential role in virtually all biological processes. Protein phosphorylation is a fast and reversible process allowing rapid signal transduction and coordinates many cellular processes through regulation of protein activity, localization, interactions, etc. The ability to rapidly add and remove phosphate groups via, respectively, kinases and phosphatases makes phosphorylation highly dynamic. Current optimized proteomics technologies allow the identification of thousands of phosphorylation sites, which can be used to infer system wide regulatory parameters. However, the high complexity of phosphorylation data in combination with the lack of functional knowledge of most phosphorylation events, severely limit the ability to understand protein activity. Therefore, alternative strategies utilizing targeted MS are gaining momentum to address specific cellular signaling events, known to be (de)regulated in disease.
Here, I will present several applications of high-resolution (integrative) proteomics as well as targeted proteomics approaches to unravel the molecular mechanisms underlying complex (disease) biology. (1-6)

References: 1. Altelaar, A.F.M., Munoz-Peralta, J. & Heck, A.J.R. (2013). Next-generation proteomics: towards an integrative view of proteome dynamics. ***Nature Reviews Genetics***, 14, 35-48 2. Brockmann M, qt al., (2017) Genetic wiring maps of single cell protein states reveal an off-switch for GPCR signaling. ***Nature***. Accepted. 3. Frese CK, et al. (2017) Quantitative Map of Proteome Dynamics during Neuronal Differentiation. ***Cell Reports***. 18(6), 1527-1542.
4. Post H., et al. (2017) Robust, Sensitive, and Automated Phosphopeptide Enrichment Optimized for Low Sample Amounts Applied to Primary Hippocampal Neurons. ***Journal of Proteome Research***, 16(2): 728-737. 5. Kemper K, et al. (2016). BRAFV600E Kinase Domain Duplication Identified in Therapy-Refractory Melanoma Patient-Derived Xenografts. ***Cell Reports***, 16(1):263-277. 6. Smit, M. A, et al. (2014). ROCK1 is a potential combinatorial drug target for BRAF mutant melanoma. ***Molecular Systems Biology***, 10 (12), 772

Keynote e Conferenze su Invito

- ANA/MAS KN 01: Cosima Damiana Calvano, Università degli Studi di Bari Aldo Moro
- ANA/MAS-KN02: Danilo Sciarrone, Università degli Studi di Messina

Advanced mass spectrometric techniques for the untargeted lipidome characterization of fibroblasts in early on-set Parkinson's disease patients

Cosima Damiana Calvano[a,b], *Marco Glaciale*[a], *Sara Granafei*[a], *Anna Maria Sardanelli*[c,d], *Luana Bellanova*[c], *Antonella Mastrorocco*[c], *Francesco Palmisano*[a,b], *Tommaso R.I. Cataldi*[a,b]

[a]Dipartimento di Chimica and [b]Centro di Ricerca Interdipartimentale SMART -Università degli Studi di Bari Aldo Moro, via Orabona 4, 70126 Bari (Italy); [c]Dipartimento di Scienze mediche di base, neuroscienze e organi di senso--Università degli Studi di Bari Aldo Moro, Piazza Giulio Cesare, 70120 Bari (Italy);[d]Dipartimento di Medicina - Università Campus Bio-Medico di Roma, Via Alvaro del Portillo 21, 00128 Roma
e-mail: cosimadamiana.calvano@uniba.it

Parkinson's disease (PD) is a progressive neurodegenerative disease involving the nigrostriatal pathway, where patients manifest dysfunction in motor symptoms when more than 50% of neurons are lost [1]. Although it is well recognized that alterations of lipid signaling and metabolism plays a significant role in many human diseases [2], little is known about the role of lipids associated with this specific disease. Recently, it has been reported that altered lipid pathways in the primary visual cortex and the anterior cingulate are possible in neurological disorders such as PD by analyzing post-mortem tissues from patients in advanced neuronal degeneration stage [3]. Such an approach, however, hinders the identification of the first neuronal changes. Thus, understanding the mechanisms of PD and identifying neuronal changes in the early phase of PD, by recurring to samples alternative to post-mortem biopsies, represents an urgent and challenging task.
According to their polygenic predisposition and environmental etiopathology [4], skin fibroblasts are now widely recognized as a useful model of primary human cells, capable of reflecting the chronological and biological aging of the patients. A lipidomics study of easily accessible primary human fibroblasts is presented here based on hydrophilic interaction liquid chromatography coupled to electrospray ionization-Fourier transform mass spectrometry, using both positive and negative polarities [5]. After testing different extraction protocols, the Bligh-Dyer method was shown to provide the largest number of recovered lipids. Thus, phospholipids (PL) from dermal fibroblasts of two unrelated PD patients with different parkin mutations and two controls were characterized by recurring to single and tandem MS measurements on a hybrid quadrupole-Orbitrap mass spectrometer. This untargeted approach enabled the identification of various PL classes as phosphatidylcholines (PC), phosphatidylethanolamines (PE), lysoPC, lysoPE, phosphatidylinositols, phosphatidylserines, sphingomyelins, mono-, di- and tri-hexosylceramides and ganglioside GM1, GM2 and GM3. To identify the main lipids and/or lipid classes involved in the pathological condition of PD, lipidomics data on a higher number of samples need to be collected and processed by multivariate statistical analyses. In this communication, an interesting set of preliminary findings will be reported and discussed.

Acknowledgments
This work was supported by *Fondazione Puglia* into the framework of the project "*Sviluppo ed uso di tecniche avanzate di spettrometria di massa per la caratterizzazione del profilo lipidomico cellulare e mitocondriale in fibroblasti controllo e di pazienti affetti da morbo di Parkinson*" PARLIAMS (Parkinson lipidome by advanced mass spectrometry).

References: 1. M.M. Wiest et al. *Curr. Opin. Lipidol*. 18 (2007) 1816. 2. T. Klockgether, *Cell Tissue Res*. 318 (2004) 115–120. 3. K. Farmer et al., *Int. J. Mol. Sci*. 16 (2015) 18865-18877. 4. J. Romaní-Aumedes et al., *Cell Death Disease* 5 (2014) 1364. 5. S. Granafei et al., *Anal Bioanal Chem* 407 (2015) 6391-6404.

Advanced Analytical Capabilities Exploiting Isotope Ratio Mass Spectrometry and Quadrupole Mass Spectrometry Coupled to Multidimensional Gas Chromatography

Danilo Sciarrone[a], *Antonino Schepis*[b], *Luigi Mondello*[a,b,c]

[a]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Polo Annunziata, Viale Annunziata - 98168 Messina; [b] Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina; [c] Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Rome, Italy.
e-mail: dsciarrone@unime.it

Isotope Ratio Mass Spectrometry (IRMS) is commonly recognized to be able to provide information about the geographical, chemical, and biological origins of substances. The ability to determine the source of substances stems from the relative isotopic abundances of the elements which comprise the material. By performing a separation prior to isotope ratio analysis, hyphenated techniques such as GC-C-IRMS, can provide isotopic analysis of a complex mixture, thereby providing additional information and higher discriminatory power. Since its introduction, the use of this analytical approach was not widespread due to a series of drawbacks related to chromatographic and isotopic issues. In fact, dead volumes due to the typical instrumental setup, requiring the combustion of the components followed by a drying step, often limit the separation efficiency, driving to an increased band broadening and peak asymmetry producing peak coelutions, thus falsify the measurements. Moreover, the reduced chromatographic performance increases the gas chromatographic isotope effect (or inverse isotopic effect) that generates GC peak not isotopically consistent because composed of lighter isotopes (^{12}C, ^{1}H and ^{16}O) that elute after the isotopomers containing heavier organic compounds because of their higher volatility. The present research deals with the development of an MDGC-MS/IRMS prototype characterized by the improved resolution capability of the heart-cut mode, exploiting two different GC stationary phases, and the simultaneous qMS and IRMS detection of the 2D chromatographic bands. The IRMS system was optimized in terms of dead volumes enabling to overcome the extra-column band broadening effect that usually affects the commercial systems. Different applications on food and flavour and fragrance samples are reported showing the enhanced performances of the prototype described.

Comunicazioni Orali

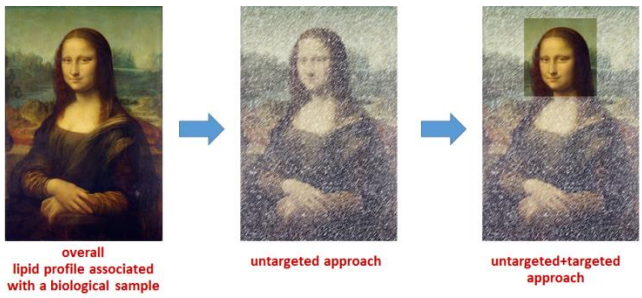
Lipostar, a Novel Platform-Neutral Cheminformatics Tool for Untargeted and Targeted Lipidomics

Laura Goracci[a]; *Sara Tortorella*[a]; *Paolo Tiberi*[b]; *Roberto Maria Pellegrino*[a]; *Alessandra Di Veroli*[a]; *Aurora Valeri*[a]; *Lucia Cesarini*[a]; *Gabriele Cruciani*[a]

[a]Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, 06123 – Perugia, Italy; [b]Affiliation and address2; [c]Molecular Discovery Ltd, Centennial Park, Borehamwood, Hertfordshire, United Kingdom.

e-mail: laura.goracci@unipg.it

Lipid impairment can occur in the pathophysiology of diseases including diabetes, obesity, heart diseases, or neurodegenerative diseases.(1,2) Consequently, lipidomics represents an emerging field with the aim of unravelling diagnostic biomarkers, new drug targets, and of rationalizing toxicity effects. Mass spectrometry (MS), due to its sensitivity and selectivity, is the elected method for qualitative and quantitative lipidomics analysis. In addition, the recent improvements in MS technologies have moved interest from targeted to untargeted approaches. Nowadays, untargeted lipidomics is still suffering for the lack of adequate computational and cheminformatics tools that are able to support the LC/MS analysis of complex lipid mixtures from biological samples. Indeed, an *in silico* aid for untargeted lipidomics must assist peak detection from raw files, data mining, statistical analysis (including prediction), and lipid identification. To address these issues, we recently developed Lipostar, a vendor-neutral high-throughput software to support targeted and untargeted LC-MS lipidomics.(3) The major innovative points in the Lipostar algorithms are the matrix-based procedure for isotopes and adducts handling, and the use of two lipid identification approaches. The first one is database-based, and searches for matches on databases of fragmented lipids. Customized databases can be generated using a specific module in the software, and trained based on the experimental results. The second identification approach is database-independent and it mimics the manual interpretation of the experimental MS/MS spectra searching for fragments that are lipid-class-specific. When Lipostar is used for pharmaceutical and medical applications, it can be also connected with the Mass-MetaSite software for the automatic identification of drug metabolites possibly extracted with lipids. A case study on drug safety assessment will be presented to describe the general Lipostar workflow.



References: 1. Ekroos, K.; Ed, R. *Lipidomics*; Ekroos, K., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012. 2. Murphy, S. A.; Nicolaou, A. *Mol. Nutr. Food Res.* 2013, *57*, 1336–1346. 3. Goracci,L.; Tortorella, S.; Tiberi, P.; Pellegrino, R. M.; Di Veroli, A.; Valeri, A.; Cruciani, G. *Analytical Chemistry*, 2017, just accepted manuscript, doi 10.1021/acs.analchem.7b01259.

Metabolic Fingerprinting of Plants and Wines

Gianluca Giorgi[a]

[a]University of Siena, Dept. of Biotechnology, Chemistry and Pharmacy, via Aldo Moro I-53100 Siena
e-mail: gianluca.giorgi@unisi.it

Metabolic fingerprinting is a high-throughput technology which mostly uses advanced methods to characterize and quantify hundreds to thousands of low molecular weight analytes simultaneously, using targeted or untargeted approaches.
In metabolomics studies, mass spectrometry (MS) is widely used being a very effective methodology for identifying, characterizing and quantifying unknowns. High sensitivity, high selectivity and high specificity are some of its main features (1).
Modern MS offers an array of technologies that differ in operational principles and performance, ranging from a wide range of ionization techniques, to high resolution and many methods for inducing dissociations of ions.
A typical strategy in metabolomics is coupling MS with chromatography. So GC-MS and LC-MS are used for studying mixtures of volatile or polar compounds, respectively.
Another approach consists of direct MS analyses of sample crude mixtures without chromatographic separations. This approach, even if less informative, provides a high throughput screening tool and allows a direct comparison between different samples.
Direct MS applicability in metabolomics is broadened by advanced instrumentation capable of high resolution, accurate mass measurements, and tandem mass spectrometry methods.
In this communication, a direct MS strategy for obtaining metabolic fingerprints of plants and wines is presented. Electrospray and paper spray ionizations have been used together with tandem MS and high resolution measurements. For identification of unknowns databases have been also used.
Different classes of compounds have been identified and interesting analogies as well as differences have been observed among homogeneous classes of samples.
A correct interpretation of the data is mandatory for avoiding errors in assigning structures.

References: 1. Z. Lei, D. V. Huhman, L. W. Sumner, *J. Biol. Chem.* **286**, 25435–25442 (2011).

Qualitative and Quantitative Characterization of a Novel DIA Method for Omics Analysis

Simona Scarpella[a]; Arthur Moseley[b]; Chris Hughes[a]; Erik J. Soderblom[b]; Keith Richardson[a]; Will Thompson[b]; Johannes PC Vissers[a]; Jason Wildgoose[a]; James Langridge[a]

[a]Waters, Wilmslow, United Kingdom; [b]Duke University School of Medicine, Durham, NC.
e-mail: Simona_Scarpella@Waters.com

Intro
In typical data independent acquisition (DIA) methods on Q-TOF instruments, the quadrupole mass filter or ion trap either operates in wide pass mode or in stepped mode with typical transmission windows in the range of 1-20Da. Here we describe a mode of DIA operation whereby a resolving quadrupole is scanned repetitively over alternating low and elevated energy scans

Methods
The m/z range of the quadrupole was continuously and repetitively scanned with data acquired using a ToF acquisition system capable of delivering 2000 ToF spectra / s. Alternate scans contain low energy data for precursor and high energy data for fragment ions. The resulting 2D data format can be processed using both commercial and open source software for identification / quantitative results

Preliminary Data
The effect of the scanning quadrupole transmission window has been investigated to assess qualitative performance. Tryptic digest standards were injected onto a LC system and separated using a 90 minute gradient. It was found that quadrupole transmission windows of 20-30 Da provided optimum protein identifications. Over 1,000 proteins were identified from a cytosolic E.coli digest standard (4% FDR). Additional evaluations of this methodology for qualitative and quantitative proteomic analyses will be made via the analyses of two disparate sample cohorts - characterization of synaptic proteomes as part of a study of developmental brain disorders, and differential analyses of protein:protein complexes of calcineurin (Aspergillus fumigatus) as a function of mechanism-of-action of several antifungal drugs.

Novel Aspect
DIA method incorporating scanning quadrupole provides greater specificity in 'Omics experiments compared with default DIA acquisition method

Qualitative and quantitative analysis of fatty acids extracted from pelagic species of the Sicilian Channel, comparison with endogenous variables

Calogera Monastero[a,b], Antonella Maggio[b], Antonio Mazzola[c], Santino Orecchio,[b] Marco Torri[a], Bernardo Patti[a], Angela Cuttitta[a]

[a] IAMC-CNR via del Mare 3 Campobello di Mazara Tp1; [b]University of Palermo(STEBICEF) viale delle Scienze Palermo2; [c]University of Palermo(STEBICEF) via Archirafi 36 Palermo 3;
linda.monastero@iamc.cnr.it

Fatty acids, especially ones in fish lipids, are very important nutritional elements for human health especially n-3 fatty acids (FAs) (1). The interest of this research has been to acquire more in-depth knowledge to evaluate the profile ω3/ω6 (GC/MS) as function of a number of endogenous variables of anchovy (*Engraulis encrasicolus)* from Sicily Channel area, and recent literature doesn't provide any results regarding this site that is a large basin economic and social importance.

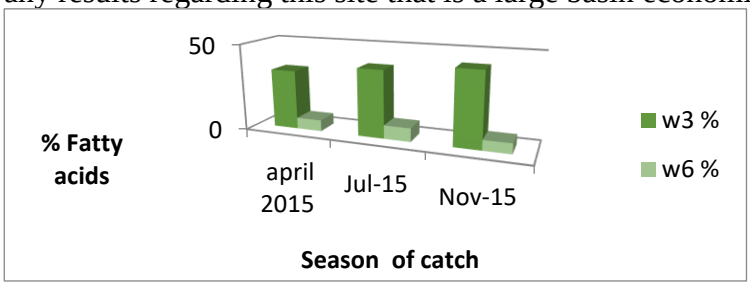


Figure 1

Figure 1 shows the variation of the main W3 and W6 in the muscle as a function of the season. The composition of fatty acids variability, depending on the season (2).The values of W3 is significantly higher ($p<0.05$) than W6 independently of the period.
Figure 2 (FAs in April- maximum spawning period) (3). The % of palmitic acid C16:0 is lower in 160-169 mm individuals (same sex) than smaller size individuals. The most important w3 shows same trend, the DHA 22:6 and EPA are higher in class 160-169 mm for same sex. This study detects a fatty acid dependence versus endogenous variables

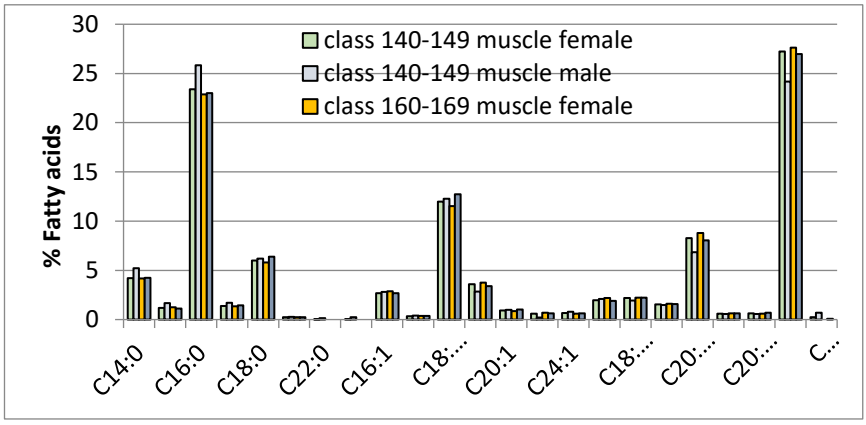


Figure 2

References:1, S. Zlatanos, K. Laskaridis. Seasonal variation in the fatty acid composition of three Mediterranean fish-sardine *(Sardina pilchardus)*, anchovy *(Engraulis encrasicolus*) and picarel *(Spicara smaris)*, *Science Direct Food Chemistry 2007*. 2: M. Pirini, S. Testi, V. Ventrella, A. Pagliarani, A. Badiari. Blue-back fish: Fatty acid profile in selected season and retention upon baking *Food Chemistry 2010;* 3: B. Patti, C. Pedroza, I. Piazza, S. Mazzola. Small pelagic fish market in the south of Sicily: socioeconomic linkages between catch volume and local consumption. Proceedings of the International Institute of Fisheries Economics and Trade Conference 2014, 7-11 July 2014, Brisbane, Australia.

LC-MS Based Metabolomics and Evaluation of the Antioxidant Activity of *Fragaria vesca* Leaves

Gilda D'Urso[a], *Cosimo Pizza*[a], *Sonia Piacente*[a], *Paola Montoro*[a]

[a]Department of Pharmacy, University of Salerno, Via Giovanni Paolo II,84084 Fisciano (SA) Italy
e-mail: gidurso@unisa.it

Wild strawberries (*Fragaria vesca*), one of the best dietary source of bioactive compounds, are well appreciated by consumers and represent an important economic source. For the strong antioxidant activity, they are of great interest also for nutritionists (1, 2). Southern Italy is an important producer of *F. vesca* berries, in fact in the Campania Region, mainly in the "Alburni" and the "Alto Sele" areas, they are recognized as a traditional food product under the name "Fragolina degli Alburni" (3).
In the recent years, also leaves of strawberry have received a lot of attention as potential source of bioactive metabolites that can be used for the formulation of pharmaceutical products (4).
In the present work, secondary metabolites of *F. vesca* leaves coming from populations spontaneously growing in the underwood (spontaneous) and in crop (cultivated) and from autochthonous and non-autochthonous germplasm of Campania region (Italy) were investigated, following an approach based on untargeted and targeted metabolomics by using the combination of LC-ESI-FT-MS analysis coupled to chemometrics data analysis like PCA (Principal Component Analysis) and PLS (Partial Least Square).
Moreover LC-MS metabolomics data were also combined with the antioxidant activity of each extract determined by TEAC assay. By this approach it was possible to classify the samples on the basis of their genetic factors and environmental conditions.
Leaves of *F. vesca* with autochthonous germplasm of Campania region showed higher antioxidant activity compared to the samples with non-autochthonous germplasm. Thus they represent a rich source of bioactive metabolites that can be used in specific food supplements and in cosmetic formulations.

References: 1 Afrin, S.; Gasparrini, M.; Forbes-Hernandez, T. Y.; Reboredo-Rodriguez, P.; Mezzetti, B.; Varela-Lopez, A.; Giampieri, F.; Battino, M. Promising health benefits of the strawberry: A focus on clinical studies. Journal of Agricultural and Food Chemistry (2016), 64(22), 4435-4449. 2. Skrovankova, S.; Sumczynski, D.; Mlcek, J.; Jurikova, T.; Sochor, J. Bioactive compounds and antioxidant activity in different types of berries. International Journal of Molecular Sciences (2015), 16(10), 24673-24706. 3. D'Urso, G.; Maldini, M.; Pintore, G.; d'Aquino, L.; Montoro, P.; Pizza, C. Characterisation of *Fragaria vesca* fruit from Italy following a metabolomics approach through integrated mass spectrometry techniques. LWT--Food Science and Technology (2016), 74, 387-395. 4. Kårlund A., Hanhineva K., Lehtonen M., Karjalainen R. O., and Sandell M. Non targeted metabolite profiles and sensory properties of strawberry cultivars grown both organically and conventionally. Journal of Agricultural and Food Chemistry (2015), 63 (3), pp 1010–1019.

Mass Spectrometry and Natural Complex Products Metabolomic Analysis

Luisa Mattoli[a], Cangi Francesca[a], Burico Michela[a], Anna Gaetano[a], Lorenzo Tafini[a], Fodaroni Giada[a], Stella Bedont[a], Sara Tamimi[a], Denise De Carli[a], Simona Propersi[a], Veronica Ercolani[a], Valentina Fiordelli[a], Enrico Flamini[a], Luca Grigi[a]

[a]*Area Ricerca Fitochimica, Aboca SpA, Italy*

Mass Spectrometry plays a relevant role as by using HRLC-MS, GC-MS, IRGC-MS, ICP-MS it is possible to characterize globally natural complex products. Untargeted metabolomic analysis by means of ESI-MS methods with multivariate statistical analysis can be an effective tool to check batch compliance, assuring constancy on the therapeutic effect. Targeted metabolomic analysis, by using a "in house" compound library (Aboca was able to build up a library of about 1000 standards) through HRLC-MS and GC-MS methods is useful to identify and quantify as much compounds as possible, achieving the correct compositional knowledge of complex natural products. We should not forget metallomic analysis by ICP-MS (also coupled with HPLC or ionic chromatograph), as inorganic salts or organometallic complexes are naturally presents and contribute to give the characteristic bioavailability to natural complex products.

Today it is mandatory to assure efficacy and safety of natural complex products through standardized processes (following Good Manufacturing Practices, GMPs) from the raw material to the formulated products. It is obvious that together with rigorous process controls, only an adequate analytical policy can help to ensure the production chain's quality.

As it is known that all the compounds present in natural complex products contributes to their multi-targeted action and consequently to their specific effect, here it is presented how a metabolomic approach get a comprehensive panorama of natural complex product's composition, useful in routine quality control (eg.: identification test and batch release, stability monitoring program, check of production process robustness).

-OMICS world: take it easy! Solutions to Advance your Metabolomics Research

Mariateresa Maldini

Application Support Specialist –OMICS, Sciex
e-mail: mariateresa.maldini@sciex.com

-OMICS is a general term for a broad discipline of science and engineering for analyzing the interactions of biological information objects in various -omes. Metabolomics, as a methodology for measuring small-molecule metabolite profiles and fluxes in biological matrices, following genetic modification or exogenous challenges, has become an important component of systems biology. Because of the comprehensive nature of metabolite measurement and the capacity to detect subtle changes in a large dataset, Metabolomics has found broad application. One of the many goals of researchers in the field of metabolomics is to analyse a large number of samples and obtain the most information in shortest times and with a little or no sample preparation time. The recent progress and developments of analysis techniques are going to satisfy this demand.
The TripleTOF® and X500R QTOF systems can collect high resolution MS/MS spectra at high MS/MS acquisition rates and have excellent low mass sensitivity, making the ideal instruments for metabolomics workflows.
In addition, improved, easy to use software, methods and libraries custom-designed for targeted customer applications are available. The breadth of data acquisition capabilities is been improved by SWATH™ Acquisition, MRMHR acquisition, information dependent high-resolution MS acquisition (IDA), and high speed MS/MS scanning.

Stable Isotopes in Fossil Remains and Environmental Reconstruction

Antonella Macrì[a], *Paola Iacumin*[b]

[a]Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università degli Studi di Parma;
[b]Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università degli Studi di Parma.
e-mail: antonella.macri@studenti.unipr.it

Molluscs precipitate their shells by adding carbonate layers in isotopic equilibrium with surrounding water solutions (1). This means that the patterns and differences in the stable isotopic composition of the carbonate shells are related to molluscs habitat and lifestyle. Here we discuss the freshwater system, focusing on the identification of some variables which influence the oxygen and carbon in the carbonate of the aquatic gastropods. $\delta^{18}O_{carb}$ mainly reflects the $\delta^{18}O$ of the water and its temperature whereas $\delta^{13}C$ is a function of dissolved inorganic carbon (DIC). Malacofauna found in archaeological context provides proxy materials for environmental and climatic reconstructions (2). The occurrence of shells in stratigraphic sequence allows us to perform a diachronic analysis of long environmental history. In order to evaluate seasonal and intraspecific variations, we present a methodological investigation and a preliminary study of bulk-shells and local sample-spot of fresh-water recent and fossil molluscs from Sudan. From this study it will be possible to see how the drying process has evolved over time along the Nilotic area.

References: 1. Fritz and Poplawski, 1974. ^{18}O and ^{13}C in the shells of freshwater molluscs and their environments. *Earth and Planetary Science Letters* 24.1: 91-98. 2. Leng M.J., Lewis J.P., 2016. Oxygen isotopes in molluscan shell: applications in environmental archaeology. *Environmental Archaeology* 21.3 295-306

Mass Spectrometry and Metallomics: a Powerful Technique to Delineate the Mode of-Action of Anticancer Metallodrugs. the Case of Oxaliplatin and its Analogues

Alessandro Pratesi[a], *Tiziano Marzo*[b], *Damiano Cirri*[a], *Luigi Messori*[a]

[a] MetMed, Department of Chemistry, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, FI, Italy; [b] Department of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 13, 56124 Pisa, Italy
e-mail: alessandro.pratesi@unifi.it

Since the discovery of the antitumor properties of cisplatin during the sixties, metal based drugs have been playing a major role in anticancer chemotherapeutic strategies. There is today a general consensus on the necessity to elucidate the mechanism of action of metal based drugs at the molecular level in such a way to rationally design novel and better anticancer metallodrugs through the so called "mechanism oriented" approach. In general, DNA is considered as the primary target for cisplatin and its close analogues (1,2) while proteins appear to play crucial roles in the transport, uptake, excretion, biodistribution, toxicity profile and resistance phenomena related to Pt drugs themselves. Even more interesting, proteins are involved in crucial aspects of the mode of action of various non-platinum anticancer agents, like ruthenium or gold complexes (3).
Metallomics is mainly concerned with the identification and characterization of all chemical species, present in a certain biological sample (a cell, a tissue or an organism), that contain the metal of interest, e.g. Pt, Au or Ru. MS represents today a fast, sensitive, specific and high-throughput tool for the analysis of biomolecules; in particular, electrospray ionization mass spectrometry (ESI-MS) potentially provides a wealth of structural and functional information mainly due to its non-destructive nature that even preserves non-covalent interactions (4). Yet, the stability of metal-protein coordination bonds may be a critical issue. This led us to build up a general protocol to test metallodrug-protein adduct stability under the typical conditions of the filter-aided sample preparation (FASP)/bottom-up procedure, ranging from the analysis of solutions containing metal-protein adducts to tandem mass spectrometry experiments. More in detail, we identified nine critical situations, either during the sample manipulations or instrumental, as a potential source of metal-protein bond impairment when using FASP operative conditions and a nanoLC-nanoESI-LTQ-Orbitrap mass spectrometer system (5).
With this experimental protocol, we successfully described the mode-of-action of some important metallodrugs. One interesting case is represented by oxaliplatin and its halido-derivatives: at variance with oxaliplatin, PtX_2(DACH) were poorly reactive toward some model proteins (Lysozyme and Ribonuclease A) while retaining a significant affinity for a representative DNA molecule (oligonucleotide). These experimental evidences, obtained through ESI-MS measurements, led us to hypothesize a structurally-related mode-of-action for these metal complexes and clearly emerged the key-role of the bidentate oxalate ligand during in recognizing the protein binding site (6).

References: 1. B. Lippert, Cisplatin: Chemistry and Biochemistry of a Leading Anticancer Drug, Wiley, New York, 1999. 2. V. Brabec, Prog. Nucleic Acid Res. Mol. Biol. 71 (2002) 1–68. 3. P.J. Dyson, G. Sava, Dalton Trans. (2006) 1929–1933. 4. K.J. Pacholarz, R.A. Garlish, R.J. Taylor, P.E. Barran, Chem. Soc. Rev. 41 (2012) 4335–4355. 5. E. Michelucci, G. Pieraccini, G. Moneti, C. Gabbiani, A. Pratesi, Luigi Messori, Talanta 167 (2017) 30–38. 6. D. Cirri, S. Pillozzi, C. Gabbiani, J. Tricomi, G. Bartoli, M. Stefanini, E. Michelucci, A. Arcangeli, L. Messori T. Marzo, Dalton Trans. 46 (2017) 3311-3317.

Chromatography-Based EA-IRMS: Redesigning the Elemental Analyzer Around Modern Chromatographic Principles to Match the Challenges of Today's and Tomorrow's Applications

Lionnel Mounier[a], *Luca Simonotti*[b], *Andreas Hilkert*[c]

[a] *Thermo Fisher Scientific, 16 avenue du Québec, Villebon-sur-Yvette 91963 Coutaboeuf Cedex, France* [b]*Thermo Fisher Scientific, Strada Rivoltana, 20090 Rodano, Milan, Italy* [c]*Thermo Fisher Scientific, Hanna-Kunath-Str. 11 28199, Bremen, Germany.*

The elemental analyzer (EA) was invented by Justus Liebig in 1830 and is deeply rooted in analytical chemistry, but the steps to make it an analytical tool for biology and geochemistry came in 1968, when Carlo Erba company replaced trapping with isothermal gas chromatography using a packed GC column, and 1980, when Tom Preston put a Carlo Erba EA onto an IRMS, inventing "continuous flow-IRMS". The technique was rapidly adopted and the work flow was extended from N to C and then S as well as to H and O. In 2016, Thermo Scientific introduced the EA-IsoLink, a revolutionary change to the elemental analyzer, where every component has been examined and either optimized or redesigned, from the auto-sampler though to the TCD. The Dumas combustion products are resolved on a GC column using variable helium flow rates and temperature ramping, and for the first time, chromatographic terms (e.g. baseline and resolution) are rigorously defined. The result is improved chromatographic performance which leads to improved isotope ratio precision for every mode of measurement and for every sample size, while at the same time improving throughput and greatly reducing helium consumption. Concrete applications of EA-IRMS will be presented.

Determination of Benzodiazepines in Beverages Using Green Extraction Methods and HPLC-UV Detection

Maurizio Piergiovanni[a], *Achille Cappiello*[a], *Giorgio Famiglini*[a], *Veronica Termopoli*[a], *Pierangela Palma*[a]

[a] DiSPeA - University of Urbino, Piazza Rinascimento 6, 61029 Urbino, Italy.
e-mail: m.piergiovanni1@campus.uniurb.it

Microextraction by packed sorbent (MEPS) and Dispersive Liquid–Liquid Micro Extraction (DLLME) with and without ultrasound assistance (UA-DLLME) were used as "green" extraction methods for the determination of benzodiazepines (BDZ) in beverages followed by HPLC-UV detection. BDZ are pharmaceutical compounds usually employed for their tranquilizing and anti-depressive effect. However, their simple availability and reduced cost make them attractive for criminal intent (1). The very low amount of sample usually available for the analyses makes the determination suitable for micro–scale extraction techniques. MEPS and DLLME are emerging techniques based on different principles, and they can be considered "green" thanks to low solvent consumption, reduced execution time and good recovery values (2,3).
MEPS, DLLME, UA-DLLME were used for the extraction of 8 BDZ (chlordiazepoxide, oxazepam, lorazepam, bromazepam, flurazepam, flumitrazepam, clobazam, and clonazepam) in three common beverages (tonic water, Spritz and red fruit juice). MEPS extraction was optimized testing various elution mixtures of solvents to yield the maximum recovery percentage. Several parameters influencing DLLME, such as type and dispersive solvent volumes, type and extraction solvent volumes, and ionic strengths were investigated and optimized to yield the highest recoveries.
The analyses were performed with a Agilent series 1100 capillary pump system with a Thermo Scientific DionexUltiMate 3400 Variable Wavelenght UV detector, 45 nL flow cell, 100 nL injection volume and an Agilent Zorbax XDB C18 (3,5 µm x 300 µm x 150 mm) column. The chromatographic separation was performed with a 4 µL/min multi-step gradient with H_2O (0,1% HCOOH) and Acetonitrile (0,1% HCOOH) and the detection was carried out at 254 nm; capillary HPLC separation with UV-detection was the analytical technique of choice because of its simplicity, robustness and wide diffusion.
The DLLME extraction was performed mixing centrifuged matrix (5500 rpm, 5 minutes), Acetone (dispersive solvent) and CH_2Cl_2 (extraction solvent) for 1 minute; then the mixture was centrifuged (5500 rpm, 5 minutes), the extraction phase was recovered, evaporated and the analyte was re-dissolved in H_2O (0,1% HCOOH). The detailed description of the method, its quantitative performance and a comparison with the MEPS results are presented. The MEPS extraction was carried out with a SGE eVol XR digital analytical syringe aspiring directly from the matrix and eluting with an Acetonitrile:H_2O 90:10 both acidified with 0,1% HCOOH. The method was validated in terms of linearity, precision, accuracy and recovery, LOD, and LOQ. Good linearity was obtained both with DLLME and MEPS with correlation coefficients (R^2) spanning from 0.996 to 0.9999. The limits of detection (LODs) of all analytes ranged from 1 ng/µL to 2.5 ng/µL. The recoveries in spiked beverages spanned from 31.7% to 69.7% for DLLME and from 62.3 % to 98.8 % for MEPS in all matrices spiked at the concentration of 20 ng/µL.

References:
1. US Department of Health and Human Services. Substance abuse and sexual assault: when drugs are used for rape. D.C. Crisis Center. www.drcc.org. 2. R. Jain, R. Singh, Trends in Analytical Chemistry 75 (2016) 227–237. 3. L. Magrini et al., Journal of Pharmaceutical and Biomedical Analysis 125 (2016) 48–53

Quantification of Plasma Proteins with Micro-LC SWATH®-MS for Biomarker Discovery in Inflammatory Bowel Disease

Marcello Manfredi[a,b], *Eleonora Conte*[b], *Elisa Robotti*[a], *Elettra Barberis*[a,b], *Fabio Gosetti*[a], *Eleonora Mazzucco*[a], *Valeria Caneparo*[c,d], *Ester Vanni*[e,f], *Santo Landolfo*[c], *Marisa Gariglio*[d], *Marco De Andrea*[c,d], *Emilio Marengo*[a,b]

[a]Università del Piemonte Orientale, Dipartimento di Scienze ed Innovazione Tecnologica, Alessandria, Italy; [b]ISALIT, Spin-off del DISIT, Università del Piemonte Orientale, Italy; [c]University of Turin, Medical School, Department of Public Health and Pediatric Sciences, Viral Pathogenesis Unit, Turin, Italy; [d]University of Piemonte Orientale, Department of Translational Medicine, Virology Unit, Novara, Italy; [e] University of Turin, Department of Medical Sciences, Gastroenterology Unit, Turin, Italy, [f] AOU Città della Salute e della Scienza - Molinette Hospital, Gastroenterology and Hepatology Unit, Turin, Italy
e-mail: marcello.manfredi@uniupo.it

Inflammatory bowel disease (IBD) is a chronic inflammatory condition of unknown aetiology that can affect any portion of the digestive tract, but most frequently the terminal ileum and/or the colon. Crohn's disease (CD) and ulcerative colitis (UC) are the most common form of IBD. Genetic factors, an abnormal immune response to microbial infections and unbalance in the gut-microbiota are thought to be involved in disease pathogenesis. The diagnosis and management of IBD still presents a number of challenges: the presence of intestinal inflammation is a primary criterion for diagnosis and differentiation from other diseases. Moreover, no definitive diagnostic test exists as a gold standard, which is made on the basis of history and physical examination, supplemented with objective findings from laboratory, radiological, endoscopic and histological studies.
The interest for the quantitation of large proteomes across multiple samples has rapidly increased during the last years, especially stimulated by the development of new instruments and tools. Low-abundant human plasma proteins are considered the most promising biomarkers for disease diagnosis and therapeutic monitoring. In this research we will present the use SWATH-MS for the reliable and fast quantitation of low-abundant plasma proteins for biomarker discovery in IBD. All the plasma samples were depleted of the 14 most abundant proteins, digested and then analyzed with SWATH-MS in order to obtain a proteomic fingerprint of each patient. Through the use of chemometric and bioinformatic tools we were able to identify several new biomarkers for the early and non-invasive diagnosis of IBD, and for the discrimination of the two subclasses of Crohn's disease and ulcerative colitis. Moreover, the application of multivariate analysis identified proteins correlations with the inflammatory index and the localization of the inflammation in the intestine. The validation and the assessment of the diagnostic power of the MS-identified biomarkers were performed on an external cohort of patients using ELISA assays.
In conclusion, we demonstrated that shotgun proteomics could have a great impact on the discovery of new biomarkers.

Improvements of Extraction and Identification Methodologies of PUFA from Algae

Ilaria Santoro[a], *Giovanni Sindona*[a], *Monica Nardi*[a], *Cinzia Benincasa*[b]

[a] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci cubo 12/C, I-87036, Arcavacata di Rende (CS)- Italy; [b] Centro di ricerca per l'olivicoltura e l'industria olearia (OLI), Contrada Li Rocchi, 87036 Rende.

e-mail: ilaria.santoro@unical.it

Marine algae are an important source of bioactive compounds like PUFA (polyunsaturated fatty acids) (2). The role of PUFA in human nutrition and disease prevention has been scientifically recognized and described. (1).

The aim of this work is the evaluation of different methodologies, suitable to be used in food and pharmaceutical industries, to properly extract lipids from algae, considering that the composition of fatty acids varies in the different algae strains.

The algae strain used in this work, Schizochytrium sp., was chosen for the high content of total polyunsaturated fatty acid in dry weight cellular.

It was shown that the highest yield of oil can be obtained by hexane/ethanol (2:8) in a soxhlet apparatus, and by CO_2 supercritical fluid extraction.

The composition of fatty acids in algae oil was evaluated by tandem mass spectrometry by ESI ionization system (3, 4).

Algae is a green sea plant used as a food and additive in many marine countries. Moreover, algae biofuels may provide a viable alternative to fossil fuels. It is becoming important in both vital application, to device modern and scientifically effective methodology to clearly identify each important component and to device suitable separation methods. The results presented here and others available from the literature indicate that it is possible to device new protocols in this important field.

References: Reference n.1.E. Abedi and M. A. Sahari; Long-chain polyunsaturated fatty acid sources and evaluation of their nutritional and functional properties; Food Sci Nutr., 2014; 2(5): 443–463. Reference n.2. H. Pereira et all; Polyunsaturated Fatty Acids of Marine Macroalgae: Potential for Nutritional and Pharmaceutical Applications; Mar. Drugs, 2012; 10 (9): 1920-1935. Reference n.3. C. Benincasa, E. Perri, E. Romano, I. Santoro, G. Sindona. Nutraceuticals from Olives Plain Water Extraction, Identification and Assay by LC-ESI-MS/MS. J Anal Bioanal Tech. 2015, 6, 274. doi:10.4172/2155-9872.1000274. Reference n.4. L. Di Donna, F. Mazzotti, I. Santoro, G. Sindona. Tandem Mass Spectrometry: A Convenient Approach in the Dosage of Steviol Glycosides in Stevia Sweetened Commercial Food Beverages. J. Mass Specrom. 2017, 52, 290-295.

Lack of Sterol Regulatory Element Binding Protein-1c Induces Alteration of Neuroactive Steroid Levels in Sciatic Nerve

Roberto Spezzano, Gaia Cermenati, Mariateresa Maldini, Silvia Pedretti, Matteo Audano, Silvia Giatti, Marzia Pesaresi, Roberto Cosimo Melcangi, Nico Mitro, Donatella Caruso

Department of Pharmacological and Biomolecular Sciences, Università degli Studi di Milano.
e-mail: roberto.spezzano@unimi.it

Sterol regulatory element-binding factor-1c (Srebf-1c) is a transcription factor that controls the synthesis of fatty acids (FAs) and triglycerids. Fatty acids and cholesterol represent the most abundant myelin lipids of the peripheral nervous system (PNS). We recently described that a genetic model of reduced fatty acid synthesis, the sterol regulatory binding factor-1c knock-out mice (Srebf-1cKO), developed peripheral neuropathy over time (1). Indeed, Srebf-1cKO mice, at two months of age, displayed a neuropathic phenotype characterized by impairment of thermal and mechanical nociceptive threshold and subtle abnormalities of small unmyelinated C fibers (1). At ten months of age, we found that Srebf-1cKO sciatic nerves showed an apparent hypermyelination of small-caliber fibers due to changes in myelin periodicity resulting in myelin instability and evident Remak bundle degeneration (1). In this contest, the role of neuroactive steroids synthesis plays an important role since it's well know that the levels of neuroactive steroids are altered in various neurodegenerative diseases, including different experimental models of peripheral neuropathy (2, 3). Previously we showed that dihydroprogesterone and 3-alpha-diol are protective agents against diabetic peripheral neuropathy by regulating the *de novo* lipogenesis pathway, which positively influences myelin fatty acid profile and consequently improved myelin structure and function (4). Based on our previous observations, to prove that neuroactive steroids and fatty acid synthesis are two metabolic pathways sensitive to each other, we decide to evaluate, for the first time, neuroactive steroids levels in sterol Srebf-1cKO male mice and compared with observations in wild type animals. Neuroactive steroids levels have been evaluated by liquid chromatography tandem mass spectrometry in plasma and sciatic nerve at two and ten months of age (5). These analyses were complemented by the gene expression profile of crucial steroidogenic enzymes in Srebf-1cKO sciatic nerve of Srebf-1cKO and relative littermate control mice. Data obtained at two months of age showed an increase of pregnenolone in sciatic nerve associated with a decrease of its first metabolite, progesterone, and further metabolites (i.e., dihydroprogesterone and isopregnanolone). High levels of testosterone and 17-β estradiol were also observed. At ten months of age, the neuroactive steroid profile showed further differences. Indeed, in addition to the changes observed at two months of age, lower levels of pregnenolone and high levels of dihydroprogesterone, tetrahydroprogesterone and isopregnanolone were detected. Furthermore, the levels of testosterone and its metabolites (i.e., dihydrotestosterone, 3α -diol and 3β -diol) were significantly decreased. These results were further corroborated by gene expression analysis, which follows the same changes. Interestingly, the levels of pregnenolone and progesterone were unmodified in plasma, suggesting a specific effect of SREBF-1c on neurosteroidogenesis. Since this peripheral neuropathy is due to altered fatty acid biosynthesis, data here reported support the concept that the cross-talk between fatty acid synthesis and neuroactive steroids, may represent a possible therapeutic strategy for peripheral neuropathy. This work was supported from the Fondazione Cariplo to R.C.M. (grant number 2012-0547) and to N.M. (grant number 2014-0991)

Reference**:** 1. Cermenati, G. et al. (2015). Cell Metab, 21, 571 -583. 2. Giatti, S. et al. (2015). Steroids, 103, 23 -30. 3. Melcangi, R. C. et al. (2014). Prog Neurobiol, 113, 56 -69. 4. Mitro N. et al. (2014). J Steroid Biochem Mol Biol. 143:115-21. 5. Caruso, D. et al. (2013). Psychoneuroendocrinology, 38, 2278 -2290.

Structural characterization of bio-functionalized gold nanoparticlesby ultrahigh resolution mass spectrometry

Simone Nicolardi[a], Yuri E.M. van der Burgt[a], Jeroen D.C. Codée[b], Manfred Wuhrer[a], Cornelis H. Hokke[c], Fabrizio Chiodo[a,b]

[a] Center for Proteomics and Metabolomics, Leiden University Medical Center, Leiden, The Netherlands; [b] Department of Bio-Organic Synthesis, Leiden Institute of Chemistry, Leiden, The Netherlands; [c] Department of Parasitology, Leiden University Medical Center, Leiden, The Netherlands

Bio-functionalized gold nanoparticles (AuNPs) have a vast field of applications. The unique properties of AuNPs functionalized with biomolecules such as peptides, proteins, lipids and carbohydrates enable innovative translational research and development in biomedicine. Current research focuses for example on the development of AuNPs for imaging, photothermal therapy, vaccination strategies and drug delivery. AuNPs in the 2-100 nm size range are typically synthesized in solution by redox reactions and can be functionalized by introducing molecules containing a thiol group to form a strong nanoparticle-sulfur bond. The structural characterization of functionalized AuNPs is challenging and requires the combination of multiple analytical techniques. Mass spectrometry (MS) has been successfully used to analyze AuNPs functionalized with small synthetic ligands with molecular mass smaller than 1000 Da. Laser desorption/ionization (LDI) and matrix-assisted LDI (MALDI) have been used in combination with time-of-flight (TOF) MS to analyzed ligands directly detached from the surface of AuNPs during the ionization process. However, TOF MS provides limited performance in terms of mass resolution and MS/MS possibilities. Thus, the analysis of AuNPs ligands has been limited to the determination of molecular mass only. To overcome these limitations, we designed an new strategy for the analysis of AuNPs based on ultrahigh resolution Fourier transform ion cyclotron resonance (FTICR) MS and a combination of LDI and MALDI. Following this strategy, we comprehensively characterized the surface chemistry of AuNPs conjugated via a thiol-ending linker to either the ovalbumin peptide (OVA 323-339), the Lewis X antigen (Galβ1-4[Fucα1-3]GlcNAcβ1) trisaccharide, the tetramannoside Manα1-2Manα1-2Manα1-3Manα1, or a mixture of both carbohydrates. We analyzed all bio-functionalized AuNPs by 15T LDI/MALDI-FTICR MS (Bruker) using 1,5-diaminonaphthalene (1,5-DAN) as a MALDI matrix. We used collision-induced dissociation (CID) to characterize the structure of pseudo-molecular ions generated by LDI/MALDI, in-depth. These included $[M+H]^+$ and $[M+Na]^+$, and importantly also $[M+Au]^+$ and $[M+2Au-H]^+$ ions which provide direct evidence for the Au-conjugation of ligands. In addition, we used our strategy to monitor proteolytic cleavage of peptides conjugated to the AuNP surface.

This study presents a novel application of ultrahigh resolution LDI/MALDI-(CID)-FTICR MS for the characterization of bio-functionalized AuNPs.

Molecularly Imprinted Materials Coupled to MALDI-TOF Mass Spectrometry for the Targeted Analysis of Peptides and Proteins

Lucia Cenci[a], *Graziano Guella*[b], *Alessandra Maria Bossi*[a]

[a] Dipartimento di Biotecnologie, Università di Verona, Strada Le Grazie 15, 3713, Verona, Italy; [b]Dipartimento di Fisica, Università di Trento, Via Sommarive 14, 38123, Povo, Trento, Italy.
e-mail: alessandramaria.bossi@univr.it

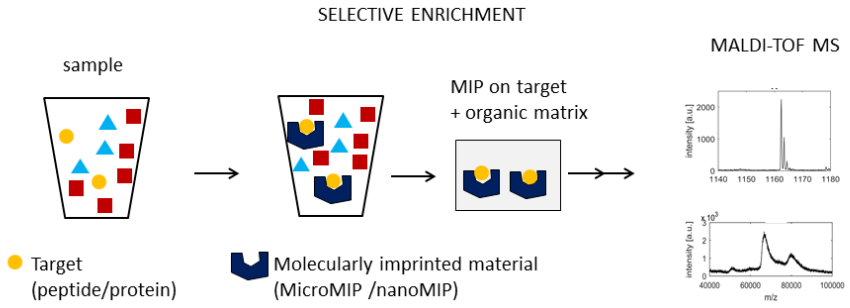
Molecularly imprinted polymers (MIPs) are a class of tailor-made biomimetic materials, prepared by template assisted synthesis: the monomers and the crosslinker are polymerized in the presence of the target analyte, called the template, thus printing onto the growing polymeric chains both the stereo and the chemical complementarity for the template. MIPs exhibit exceptional recognition properties for the template (being this a small molecule, a peptide or even a protein) with reported affinities and selectivity of the par of natural antibodies[1-3]

With the aim at improving the analytical methodologies meant for targeted proteomics and clinical applications, we propose the development of a flexible analytical platform based on the integration of MIPs to MALDI-TOF mass spectrometry (MS) for targeted protein analysis and characterized by selective enrichment,[4] high sensitivity and selectivity and short analysis times.

Libraries of micro and nano-MIPs addressed at the recognition of peptides and proteins, including responsive MIP-materials, were synthesized by radical polymerization of acrylamido-based monomers. The prepared materials were characterized physico-chemically, showing ~2 µm microMIPs and ~50 nm nanoMIPs. The MIP compositions were confirmed by XPS analysis. The binding isotherms demonstrated nanomolar affinities for the templates. At last, the micro- and nanoMIP materials were coupled to MALDI-TOF-MS.

The analytical performance of the MIP/MALDI-TOF-MS was studied by challenging the system with selected peptides and proteins, at concentrations spanning from the nano- to the pico-molar; in model solution and in real biological specimens.[5,6]

The results demonstrated the ability of the MIP/MALDI-TOF-MS hyphenation to detect in short times (few minutes) pico- to femto-moles of the target analyte straight from serum samples, with minimal sample handling, hence proving the strength of coupling micro- and nano-MIP materials to MALDI-TOF-MS, opening up innovative analytical perspectives.



References: 1. Alexander C. et al. J. Mol. Recognit. 19 (2003) 106–180.; 2. Bossi et al. Biosens. Bioelectronics 22 (2007) 1131-1137.; 3. Hoshino Y. et al. J. Am. Chem. Soc. 130 (2008) 15242–3.; 4. Urban PL et al. Mass Spectrom. Rev. 30 (2011) 435–478.; 5. L. Cenci et al. J. Mol. Recognit. 29 (2016) 41–50.; 6. Bertolla et al. ACS Appl. Mater. Interfaces 2017, 9, 6908−6915.

Unknown and non-target analysis to determine pesticides in fruit and vegetables by means of UHPLC-HRMS (Orbitrap)

Rossana Scarpone[a], *Roberta Rosato*[a], *Federico Bacá*[b], *Manuel Sergi*[c], *Dario Compagnone*[c]

[a] Istituto Zooprofilattico Sperimentale dell'Abruzzo e del Molise "G. Caporale", 64100 Teramo; [b] Affiliation and address2; [c] University of Teramo, Faculty of Bioscience and Technology for Food, Agriculture and Environment, 64100 Teramo.

e-mail: r.scarpone@izs.it

In the last years, high-resolution techniques have enhanced the number of pesticides and pesticide-related metabolites that can be detected in food. Conventionally, the detection of pesticides in food by means of both non-target and unknown screening methods has been accomplished by either GC-HRMS or LC-HRMS followed by data processing with specific, but limited, compound databases developed by companies working in the field (1). Empirical formulas of the molecules under investigation can be generated through a combination of parameters such as mass accuracy, isotopic clusters and ion fragments in order to be used for researches on online databases (e.g. ChemSpider).
This work reports a chromatographic-alignment mass-spectrometry-based approach to detect and identify pesticides and pesticide-related metabolites by comparison of matrix blank chromatograms ("CONTROL") with unknown sample chromatograms ("SAMPLE").
An UHPLC/Orbitrap system was used to carry out five chromatographic runs of both blank matrices (CONTROL) and sample matrices (SAMPLE) and a single FullScan-ddSM^2 chromatographic run.
The software calculated a SAMPLE to CONTROL *ratio* taking the average intensity of signals originated from unknown sample chromatograms and the signals originated from matrix blank chromatograms. SAMPLE/CONTROL ratios and p-values calculated on the SAMPLE signals were used to establish a threshold to filter out non-significant values. The unknown pesticides were then identified referring to online databases such as ChemSpider/Pesticides common Names, EPA Toxcast and FDA.
A specific software was used to confirm suggested compound identities and structures based on observed fragmentation patterns. All metabolites and/or degradation products of pesticides that can possibly be found in the samples can be investigated after identification through the method described above.
Quality control approach to test this method was made using SANTE/11945/2015 document as reference. A team of research unrelated to this experiment spiked samples of stone fruits with 36 different pesticides showing a wide range of physical-chemical properties thereby ensuring all compound classes detectable by LC-MS to be represented.
This method was compared to both a screening target method that uses a 350 compounds homemade database with 350 compounds and non-target method that uses a database with 650 pesticides from.
The results provided an unambiguous identification and structural characterization of the compounds based on accurate mass measurement and informative fragmentation spectra resulting in no false positive and no false negative data. Moreover, this method allowed to detect and identify two metabolites undetected by both target and non-target approach.

References: 1. Masiá, A., Suarez-Varela, M.M., Llopis-Gonzalez, A., Picó, Y., Determination of pesticides and veterinary drug residues in food by liquid chromatography-mass spectrometry: A review, 2016, Analytica Chimica Acta, 936 (14), 40-61.

From Ascorbic Acid to Furan Molecules: A Theoretical and Experimental Study on the Gas Phase Acid Catalyzed Degradation of Vitamin C

Andreina Ricci[a], *Paola Cimino*[b], *Anna Troiani*[c], *Federico Pepi*[c] *Stefania Garzoli*[b], *Chiara Salvitti*[c] *and Vincenzo Barone* [d]

[a] Department of Math and Phys, Second University of Naples, Viale Lincoln,5, 81100 Caserta, Italy [b] Department of Chemistry and Drug Technologies, 'Sapienza' University of Rome, P.le A. Moro 5, 00185 Rome, Italy [c] Department of Pharmaceutical Science University of Salerno, Via Giovanni Paolo II-84084-Fisciano (Sa) Italy [d] Scuola Normale Superiore, Piazza Cavalieri 7, I-56126 Pisa, Italy.
e-mail: Andreina.ricci@unina2.it

Degradation of L-ascorbic acid (L-AA) occurs into two types of reactions, named the non-oxidative and the oxidative. The main difference between these two pathways is that furfural is more easily produced through the former. It should be noted that the expression non-oxidative refers solely to the nature of the initial step, since subsequent transformations may involve various oxidation steps. Indeed, the oxidative pathway describes the reaction which involves as an initial step the oxidation of L-ascorbic acid to dehydro-L-ascorbic acid. Likewise, the non-oxidative pathway relates to the direct decomposition of L-ascorbic acid with exclusion of dehydro-L-ascorbic acid as an intermediate structure. In1995, furan and its derivatives were classified by the International Agency on Cancer Research (IARC) in the group 2B, as possibly carcinogenic to humans.

Since the first report in 1933, the formation of furfural from L-AA in strong acid media has been confirmed by many workers and some reaction mechanisms for the formation of furfural from L-AA have been proposed. However, none of them seems to be acceptable as the mechanism taking place in ordinary food stuffs.

Here we report on the gas-phase investigation performed by a joined mass spectrometric and theoretical approach on the acid catalysed mechanism for the formation of furan compounds in the non-oxidative degradation of L-AA. According to this approach, gaseous protonated ascorbic acid ions, $[C_6H_8O_6]H^+$, at m/z 177, were generated by Electrospray Ionization Mass Spectrometry of an ascorbic acid solution. The $[C_6H_8O_6]H^+$ ionic reactants at m/z 177 were previously structurally characterized as the ascorbic acid molecule protonated at the O2 carbonyl oxygen atom.(1)

They were subjected to collisionally activated decomposition (CAD) in order to induce the gas phase unimolecular degradation pathway of protonated ascorbic acid.

The degradation pathway emerging from the CAD mass spectrum of the precursor ion at m/z 177 shows a twofold dehydration step, 177→159 and 159→141 followed by the elimination of an $HCOOH/CO_2$ moiety, 141→95/97, leading to the formation of furanic products.

Energy Resolved CAD mass spectra allowed to obtain informations on the relative energies of degradations steps. Experimental results were compared with those of a theoretical investigation performed at B3LYP/6-31+G(d,p) level of theory highlighting the most favourable decomposition pathway. The mechanism leading to furan compounds involves dehydration, hydrolysis of the lactone ring followed by decarboxylation.

References: 1. Ricci A, Pepi F, Cimino P, Troiani A, Garzoli S, Salvitti C, Di Rienzo B, Barone V. Vitamin C: an experimental and theoretical study on the gas-phase structure and ion energetics of protonated ascorbic acid J Mass Spectrom. **2016** 51(12):1146-1151. doi: 10.1002/jms.3848.

Liquid-EI (LEI) Atmospheric Pressure Mechanism for the Introduction of Liquid Streams into an Unmodified Electron Ionization Source of a Mass Spectrometer

Veronica Termopoli[a], *Pierangela Palma*[a], *Giorgio Famiglini*[a], *Maurizio Piergiovanni*[a], *Achille Cappiello*[a]

[a]LC-MS Laboratory, Department of Pure and Applied Sciences, Piazza Rinascimento 6, Urbino.
e-mail: veronica.termopoli@uniurb.it

We have combined, for the first time, an atmospheric pressure gas-phase conversion mechanism with new ceramic coatings to create an innovative interface, called Liquid-EI (LEI) (1). LEI is based on electron ionization (EI) but differs from previous attempts; the vaporization of solutes and mobile phase takes place at atmospheric pressure into a specifically designed region, called the "vaporization micro-channel", before entering the high-vacuum ion source. The interface is completely independent from the rest of the instrumentation, and can be adapted to any gas chromatography-mass spectrometry (GC-MS) system, as an add-on for a rapid LC-MS conversion. A ceramic liner, placed inside the vaporization micro-channel, acts as an inert, 'non-stick' vaporization surface, speeding up the gas-phase conversion of large molecules while lessening possible memory effects.
EI is an unparalleled, well-established tool for the identification of unknown gas-phase molecules. Its extension to a liquid phase, without the drawbacks and limitations that troubled this hybrid combination to date, provide the same unique advantages (library searchable mass spectra, robustness, negligible matrix effects) to LC amenable compounds, opening the door to new, challenging LC-MS applications. Deactivated silica coatings help to release the heaviest compounds to the gas-phase, improving vaporization efficiency and reducing high-temperature contact time for the most labile substances, bridging the gap between the world of classic LC-MS and GC-MS.

References: 1. Termopoli, V., Famiglini, G., Palma, P., Piergiovanni, M., Cappiello, A. *Anal Chem* (2017) 89 (3), pp 2049–2056

Selective Gas-Phase Conversion of D-Fructose to 5-Hydroxymethylfuraldehyde Through a Base-Assisted Dehydration Process

Chiara Salvitti[a], *Andreina Ricci*[b], *Federico Pepi*[a], *Stefania Garzoli*[a], *Anna Troiani*[a], *Giulia De Petris*[a], *Marzio Rosi*[c]

[a] Dipartimento di Chimica e Tecnologie del farmaco, Università di Roma "Sapienza"; [b] Dipartimento di Matematica e Fisica, Università degli studi della Campania "Luigi Vanvitelli"; [c] Dipartimento di Ingegneria civile e ambientale, Università di Perugia and ISTM-CNR.
e-mail: chiara.salvitti@uniroma1.it

5-hydroxymethylfuraldehyde (5-HMF) is the main product of the thermal acid-catalysed dehydration of monosaccharides and together with other furan compounds is considered a platform molecule for the production of chemicals and fuels. Identifying alternative catalytic strategies to synthesize 5-HMF represents a key-step to increase reaction selectivity and reduce degradation-by-product yields. In this regard, mass spectrometry has proved to be an useful tool for studying reaction mechanisms in absence of solvent molecules. This approach has already been employed to investigate the acid-catalysed D-glucose and D-fructose dehydration mechanism, highlighting the formation in the gas-phase of a 5-HMF protomers and isomers mixed population (1,2). In this work the effect produced by nitrogen-containing bases on the D-fructose dehydration reaction has been evaluated using tandem mass spectrometry. Ionic complexes formed by the protonated sugar and a nitrogen base were allowed to undergo collision-induced dissociation (CID) in an ion trap mass spectrometer. The dehydration process was followed step-by-step by isolating in turn the resulting ionic intermediates that still retain the attached bases depending on their proton affinity values. The sequential fragmentation leads to the formation of $[C_6H_6O_3]H^+$ ions corresponding to a pure protonated 5-HMF population when the base loss occurs as the last reaction event (Figure 1). This evidence demonstrates the existence of a selective and effective base-assisted mechanism. Theoretical calculations are in progress in order to: i) elucidate the structures of the starting reactant ion and of the intermediates ii) validate a feasible reaction mechanism.

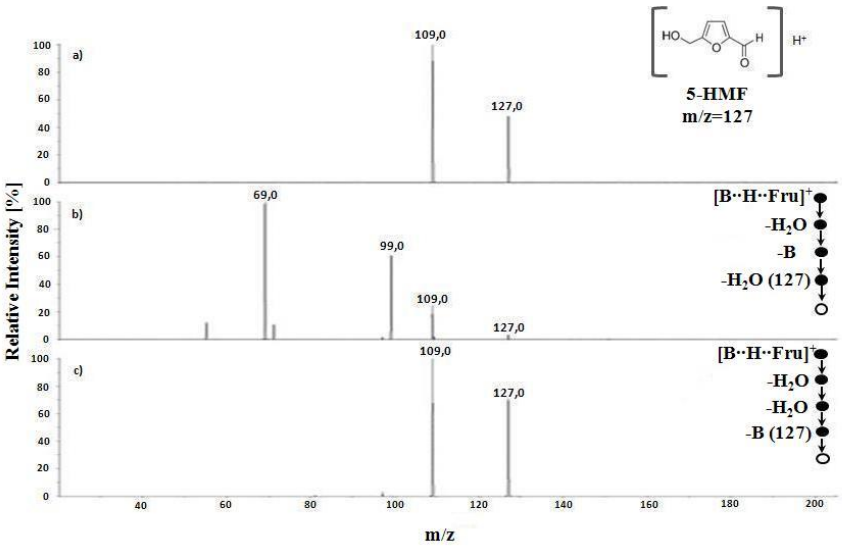


Fig. 1 CID mass spectra of a) protonated standard 5-HMF, b) ions at m/z 127 obtained after a premature base loss and c) ions at m/z 127 arising when the base loss occurs as the last reaction event.

References: 1. A. Ricci, B. Di Rienzo, F. Pepi, A. Troiani, S. Garzoli, P. Giacomello, *J. Mass Spectrom.* **2015**, *50*, 228-234. 2. F. Pepi, A. Ricci, S. Garzoli, A. Troiani, C. Salvitti, B. Di Rienzo, P. Giacomello, *Car. Res.*, **2015**, *413*, 145-150

Comunicazioni Poster

Metabolic profiling of Sicilian Opuntia ficus indica Mill. flowers

Alfredo Bottone[a], Antonietta Cerulli[a], Milena Masullo[a], Paola Montoro[a], Cosimo Pizza[a], Sonia Piacente[a]

[a]Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA).
e-mail: abottone@unisa.it

Opuntia ficus indica Mill. (Cactaceae) is a succulent plant native of Mexico and widely spread all over the world thanks to its capability to adapt itself to almost all types of climates. It is constituted by a modified stem made up of cladodes covered by thorns, with yellow flowers and juicy fruits of different colors (1). Even if spontaneous, it is largely cultivated for the production of its fruits, consummed fresh or dried. In Sicily, to increase the production of the fruits and also to enhance their quality, the flowers appearing during the first blooming are chopped off (a process called "scozzolatura"), in order to induce a second blooming, leading to the growth of bigger and more numerous fruits (2). Since the disposal of the discarded flowers represents a further expense to the production costs, this study is aimed at evaluating the metabolic profile of the polar fraction of the Sicilian *O. ficus indica* flowers, in order to exploit such by-products as a source of phenolics with anti-oxidant activity to employ in nutraceutical and cosmetic fields.
The hydroalcholic extract of the flowers was firstly submitted to LC-MS experiments to obtain a complete profile of the secondary metabolites and successively purified by size-exclusion chromatography and by RP-HPLC. The structures of the isolated compounds were elucidated by NMR experiments and confirmed by MS experiments. Moreover, the quantitative analysis of the major compounds was carried out by UHPLC-ESI-QqQ-MS/MS experiments using the Multiple Reaction Monitoring (MRM) approach. Finally, the total phenolic content of the extract was evaluated by Folin-Ciocalteu assay, as well as the radical scavenging activity by DPPH and TEAC assays.
The obtained results suggested that the Sicilian *O. ficus indica* flowers are a rich source of phenolic compounds with anti-oxidant activity, to be employed in the production of cosmetic formulations rich in polyphenols and in the manifacture of dietary supplements.

References: 1. Griffith, M. P. The origins of an important cactus crop, *Opuntia ficus indica* (Cactaceae): new molecular evidence. Am. J. Bot. 2004, 91(11), 1915-1921. 2. Inglese, P.; La Mantia, T.; Chessa, I.; Nieddu, G. Evolution of endogenous gibberellins at different stages of flowering in relation to return bloom of cactus pear (*Opuntia ficus-indica* L. Miller). 3rd International Congress on Cactus Pear and Cochenille", Acta Horticulturae. 1997, 438, 65-82.

Multiple MS approaches for the identification of new psychoactive substances, a case report: identification of deschloroketamine in seized sample from Genova and Torino

Anna Maria Caputo[a], *Damiano Ricci*[a], *Serena Detti*[a], *Sabino Napoletano*[a], *Valter Fraioli*[a], *Claudia Canali*[b], *Antonietta Lombardozzi*[c], *Morela Strano*[c], *Anna Calì*[d], *Daniel Jardines*[e]

[a] Ministry of Interior, Dep. of P. S., Forensic Science Service of Italian National Police, Via Tuscolana 1548, 00173 Rome, Italy; [b] Regional Forensic Office of Italian National Police, Corso Saffi,37,16128, Genova, Italy; [c]Interregional Forensic Office of Italian National Police, via Veglia, 44, 10136 Torino, Italy; [d] Agilent Technologies Italia S.p.A, Via Vincenzo Lamaro, 13, 00173 Rome (RM), Italy; [e]Antidoping Laboratory of Rome, Italian Sports Medicine Federation, Largo Giulio Onesti 1, 00197 Rome (RM), Italy.
e-mail: annamaria.caputo@interno.it

The spread of new psychoactive substances is facilitated by new technologies: a large range of social networks, blogs and fora are being used to share NPS-related opinions, information, links, and experiences; moreover electronic currencies and anonymous transaction infrastructures were developed (1). This phenomenon is constantly monitored by law enforcement agencies and their resulting investigation activities require timely and qualified technical support for the repressive action. This work presents the analytical approach that led to the identification of deschloroketamine. This molecule, not directly classified as illicit drug by the Italian law, has similar hallucinogenic effects of ketamine (2). Deschloroketamine, along with other alkylarylcyclohexylamines (i.e. methoxetamine), is among the substances of interest in drugs abusers and vendors, as confirmed by a recent analysis of trends on cryptomarket fora (3).

In the same period, two cases from Genova and Torino required technical support for the analysis of similar white powder samples. Investigation activities suggested samples were drug of abuse, but first GC-MS analysis did not allow any identification and the same analytical response was recorded for both samples. The mass spectrum obtained in full scan mode showed intense peaks at m/z 146, 175 and weak signal at m/z 203, so nominal mass was difficult to attribute. The same analytical method was exported to GC-QTOF instrumentation which provided accurate masses of the previously recorded peaks: in particular m/z 203.1306 at relatively low intensity. Only through the LC-HRMS analysis molecular weight of the unknown substance was attributed with greater certainty: an intense signal at m / z 204.1391 was detected by modulating suitably ionization and collision energy. Mass spectrum allowed to generate the empirical formula C13H17NO. Subsequent MS/MS fragmentation studies both in GC and LC-HRMS enabled to characterize the unknown molecule. Molecular Structure Correlator (MSC) was used: the software attempt to explain each observed fragment ion into a proposed structure using a “systematic bond-breaking” approach.

Identification of deschloroketamine in both cases was performed also through the information exchange network “National Early Warning System” activated by Department for Antidrug Policies-Presidency of the Council of Ministers. Data were compared with similar cases presented in Puglia and Liguria in 2015; recent studies have been made relating to further cases presented in Veneto (4). The essential features of the analytical approach presented were speed of the analysis and relative ease and suitability of data interpretation using MSC software and available databases: this allowed to promptly provide required technical support for the prosecution of investigations.

References: 1. Hum. Psychopharmacol Clin Exp 2015; 30: 302–318. 2. Drug Test. Analysis 2014; 6, 614–632. 3. Int. J. of Drug Policy 2017; 40: 102–110 4. Rapid Commun. Mass Spectrom. 2016, 30: 151–160.

Mass Spectrometry-Based Lipidomics in Different Grape Varieties

Donatella Caruso[a], Mariateresa Maldini[a], Roberto Spezzano[a], Flavio Giavarini[a], Nico Mitro[a], Riccardo Flamini[b],

Department of Pharmacological and Biomolecular Sciences, Università degli Studi di Milano, via Balzaretti, 9, 20133 Milano, Italy; [b] Council for Agricultural Research and Economics – Viticulture (CREA-VIT), Viale XXVIII aprile 26, 31015 Conegliano (TV), Italy

Lipids are a large class of biomolecules with a wide range of biological activities. In plant cells, they act as storing energy, signalling molecules and as structural components of cell membranes. Furthermore, are also widely known their beneficial health effects since they prevent cardiovascular diseases (1,2).

Corvina, Raboso Piave, and Glera are grape varieties cultivated in Veneto and used to produce important Italian wines, such as Amarone and Recioto, Raboso and Raboso Passito, Prosecco.

To the best of our knowledge, reports on lipidomic profiles of these grapes are very poor, and the objective of this study was to characterize the lipid pattern, namely phytosterols (PSs), fatty acids (FAs) and phospholipids (PLs), in skin and seed extracts of these grape varieties. The study was performed by using different liquid chromatography-mass spectrometry approaches.

For phytosterols analysis, a HPLC-APCI-IT-MS/MS method was developed for determination of campesterol and stigmasterol. Fatty acids and phospholipids were analysed by using HPLC-ESI-QqQ-MS/MS instrument in SIM and MRM mode, respectively.

Different contents of PSs, FAs, and PLs were found in skin and seeds. In general, higher PSs were found in seeds. The varieties showed different profiles: major FA content was found in Glera and Raboso Piave seeds, and in Corvina and Glera skins; the highest PSs were found in Glera seeds and skin. These preliminary results indicate Glera is a grape variety richer in lipids.

Respect all page layout in the template, abstracts with altered layout will be returned to author for correction.

Insert references in brackets as follows: (1) (1,2,3) and add reference list at the bottom of the abstract using justified Times New Roman 10, with line-spacing 1. As indicated below:

References: 1. Della Corte A. *et al.*, *Talanta*, (**2015**), 140; 52-61. 2. Garavaglia *et al.*, *Nutrition and Metabolic Insights* (**2016**) 9, 59–64.

LC-MS/MS Analysis of a Water Cherry (*Prunus Avium* L.) Extract with Promising Radiomodulating Effects

Giuseppina Crescente[a], *Simona Piccolella*[a], *Paola Nocera*[b], *Lorenzo Manti*[c], *Severina Pacifico*[a]

[a] Department of Environmental Biological and Pharmaceutical Sciences and Technologies, University of Campania "Luigi Vanvitelli", Via Vivaldi 43, I-81100 Caserta, Italy; [b] Department of Chemical Sciences, University of Naples Federico II, Via Cinthia, 26, I-80126 Naples, Italy; [c] Department of Physics "E. Pancini", University of Naples Federico II, via Cinthia, I-80126 Naples, Italy.
e-mail: giuseppina.crescente@unicampania.it

Human exposure to ionizing radiation is ubiquitous because of its natural occurrence and widespread use in diagnostics and therapy. Therefore, developing radioprotectors and radiorecovery drugs is of great importance in view of their potential application during both planned radiation exposure (e.g. radiotherapy) and unplanned radiation exposure (e.g. in the nuclear industry, natural background radiation emanating from the earth or other sources) (1). To this purpose, several natural plant products have been investigated (2) and antioxidant plant extracts, as well as their fractions and isolated constituents, have been shown to display important radioprotective properties. On the other hand, certain types of cancers show an inherent resilience to radiation therapy, due to pleiotropic genetic control, stem cell niches and oxygen-depleted necrotic regions (3). This has prompted a long-standing quest for radiosensitizing drugs, including many based on plant-derived polyphenols (4). Based on our previous data, showing that high doses of cherry polyphenol extracts (> 200 μg/mL) were able to target *in vitro* redox mitochondrial activity of human neuroblastoma cells (5), using different extraction conditions, involving ultrasound assisted maceration (UAM), the formulation of an aqueous extract (PaDRw) from fruits of *Prunus avium* cv. Della Recca was achieved. PaDRw exerted promising radiomodulatory properties towards neuroblastoma SH-SY5Y cell line irradiated with four graded x-ray doses (0, 0.5, 2, and 4 Gy). In fact, it was able to act as radioprotector at lower tested doses (25 and 50 μg/mL), and radiosensitizer at 400 and 500 μg/mL dose levels. To comprehensively identify the metabolites responsible of PaDRw capability, the extract underwent a simple fractionation protocol, based on the use of the Amberlite XAD-4 non-ionic polymeric resin. The simplification of the complex sample in two fractions, coupled to LC-UV-MS/MS techniques, proved to be efficient also in the disclosure of lower constituents. Quantitative analysis demonstrated that about 63% of the whole PaDRw extract was constituted by hexitol, followed by ~22.8% of fructose and ~10.7% of glucose. Phenol compounds, mainly chlorogenic acids and flavonoids, which accounted only for about 2.2%, were hypothesized to be the main actors in PaDRw-induced radiomodulation.

References: 1. Arora R., Gupta D., Chawla R., Sagar R., Sharma A., Kumar R., Prasad J., Singh S., Samanta N., Sharma R.K., Radioprotection by plant products: present status and future prospects, Phytother Res. 19 (2005) 1–22. 2. Kuntić V.S., Stanković M.B., Vujić Z.B., Brborić J.S., Uskoković-Marković S.M., Radioprotectors - the evergreen topic, Chem. Biodivers. 10 (2013) 1791–1803. 3. Peitzsch C., Perrin R., Hill R.P., Dubrovska A., Kurth I., Hypoxia as a biomarker for radioresistant cancer stem cells, Int. J. Radiat. Biol. 90 (2014) 636–652. 4. Garg A.K., Buchholz T.A., Aggarwal B.B., Chemosensitization and radiosensitization of tumors by plant polyphenols, Antioxid Redox Signal. 7 (2005) 1630–1647. 5. Pacifico S., Di Maro A., Petriccione M., Galasso S., Piccolella S., Di Giuseppe A.M.A., Scortichini M., Monaco P., Chemical composition, nutritional value and antioxidant properties of autochthonous *Prunus avium* cultivars from Campania Region, Food Res. Int. 64 (2014) 188–199.

LC-ESI/LTQOrbitrap/MS/MS^n analysis of the polar lipids of *Corylus avellana* (cultivar "Tonda di Giffoni") hazelnut kernel

Napolitano Assunta[a], *Cerulli Antonietta*[a], *Pizza Cosimo*[a], *Piacente Sonia*[a]

[a] Università degli Studi di Salerno - Via Giovanni Paolo II, 132-I-84084, Fisciano (SA), ITALY.
e-mail: anapoli@unisa.it

Corylus avellana L. (Betullaceae) is the most famous hazelnut tree. The hazelnut world production accounts for about 800,000 tons, with Turkey being the leading producer (64%), followed by Italy (13%) (1). Hazelnuts are typically consumed as whole nuts (fresh or roasted) or as ingredient for a great variety of bakery, candy and chocolate products. The kernel of the hazelnut seed is edible and has a thin, dark brown skin, which sometimes is removed before cooking.
Hazelnuts contain a great number of bioactives and health-promoting components. They are highly nutritious and contain macronutrients (lipids, proteins and carbohydrates), micronutrients (minerals and vitamins), and various phytochemicals (2). Thereby, due to their nutritional and nutraceutical properties, Food and Drug Administration (FDA) has recognized hazelnuts as "heart-healthy" foods, and several research groups reported the benefits of inclusion of hazelnuts in the human diet (3). In particular, the oil extracted from hazelnuts has proved to be able to decrease cholesterol levels in blood and to control adverse effects of hypertension. This may be due to the favourable hazelnut oil lipid profile, highly rich in MUFA (primarily oleic acid), PUFA (primarily linoleic acid), tocopherols and sterols (4). In Italy there are two hazelnut cultivars registered with the mark of Protected Geographical Indication (PGI), "Nocciola del Piemonte" and "Tonda di Giffoni (TG)". The latter is a cultivar of the Campania region, which contributes largely to the production of national hazelnut, of which it accounts for about a third.
Considering that until now no comprehensive analysis is available about polar lipids of 'TG' *C. avellana* hazelnut kernel, in the present work a detailed characterization of the lipids present in the *n*-butanol extract of fresh 'TG' hazelnut kernels (without skin) was performed by using an analytical approach based on high-performance liquid chromatography coupled to multiple-stage linear ion-trap and orbitrap high-resolution mass spectrometry (LC-ESI/LTQOrbitrap/MS/MS^n). Considering the remarkable structural diversity of lipid classes, differing in their ionization capacity and producing polarity-dependent forms of molecular anions and cations, both negative and positive electrospray ionization were used. This methodological approach enabled the analysis of a wide range of compounds from oxylipins to intact high molecular weight lipids, such as phospholipids, sphingolipids, no- and diglycosylated monoglycerides, and sulfoquinovosyldiacylglycerols.

References: 1. S. Klockmann, E. Reiner, N. Cain, M. Fischer. J. Agric. Food Chem. 2017, 65, 1456−1465. 2. C. Alasalvar, B.W. Bolling. British Journal of Nutrition. 2015, 113, S68–S78. 3. C. Alasalvar, M. Karamacä, R. Amarowicz, F. Shahidi. J. Agric. Food Chem. 2006, 54, 4826-4832. 4. T. Delgado, R. Malheiro, J.A. Pereira, E. Ramalhosa. Industrial Crops and Products. 2010, 32, 621-626.

Elenco degli Autori

*Indica l'autore presentatore

Mitro Nico	MASOR14
	MASPO03
Mohammed Shabaz	MASPL03
Monastero Calogera*	MASOR04
Mondello Luigi	ANA/MASKN02
Montoro Paola	MASOR05
	MASPO01
Moseley Arthur	MASOR03
Mounier Lionnel*	MASOR10
Napoletano Sabino	MASPO02
Napolitano Assunta*	MASPO05
Nardi Monica	MASOR13
Nicolardi Simone*	ANA/MASOR01
Nieuwenhuis Joppe	MASPL03
Nocera Paola	MASPO04
Orecchio Santino	MASOR04
Pacifico Severina	MASPO04
Palma Pierangela	MASOR11
	ANA/MASOR05
Palmisano Francesco	ANA/MASKN01
Patti Bernardo	MASOR04
Pedretti Silvia	MASPL01
	MASOR14
Peeper Daniel S.	MASPL03
Penning Renske	MASPL03
Pepi Federico	ANA/MASOR04
	ANA/MASOR06
Perini Matteo	MASPL02
Pesaresi Marzia	MASOR14
Piacente Sonia	MASOR05
	MASPO01
	MASPO05
Piccolella Simona	MASPO04
Piergiovanni Maurizio*	MASOR11
Piergiovanni Maurizio	ANA/MASOR05
Pizza Cosimo	MASOR05
	MASPO01
	MASPO05
Post Harm	MASPL03
Pratesi Alessandro*	MASOR09
Raaben Matthijs	MASPL03
Raaijmakers Linsey	MASPL03

Ricci Andreina*	ANA/MASOR04
Ricci Andreina	ANA/MASOR06
Ricci Damiano	MASPO02
Richarson Keith	MASOR03
Robotti Elisa	MASOR12
Rosato Roberta	ANA/MASOR03
Rosi Marzio	ANA/MASOR06
Saez Enrique	MASPL01
Salvitti Chiara*	ANA/MASOR06
Salvitti Chiara	ANA/MASOR04
Santoro Ilaria*	MASOR13
Sardanelli Anna Maria	ANA/MASKN01
Scarpella Simona*	MASOR03
Scarpone Rossana*	ANA/MASOR03
Schepis Antonino	ANA/MASKN02
Schmidlin Thierry	MASPL03
Sciarrone Danilo*	ANA/MASKN02
Sergi Manuel	ANA/MASOR03
Simonotti Luca	MASOR10
Sindona Giovanni	MASOR13
Soderblom Erik	MASOR03
Spezzano Roberto*	MASOR14
Spezzano Roberto	MASPO03
Stickel Elmer	MASPL03
Strano Morela	MASPO02
Stucchi Riccardo	MASPL03
Tafini Lorenzo	MASOR06
Tamimi Sara	MASOR06
Termopoli Veronica*	ANA/MASOR05
Termopoli Veronica	MASOR11
Thompson Will	MASOR03
Troiani Anna	ANA/MASOR04
	ANA/MASOR06
Torri Marco	MASOR04
Van Der Burgt Yuri E.M.	ANA/MASOR01
Van Gelder Charlotte A.G.H.	MASPL03
Vanni Ester	MASOR12
Visser Johannes	MASOR03
Wagner Björn	MASOR01
Wildgoose Jason	MASOR03
Wuhrer Manfred	ANA/MASOR01