47 Congresso Nazionale di CHIMICA INORGANICA

BARI
9-12 Settembre 2019
Aula Magna "Aldo Moro"
Aula "Gaetano Contento"
Dipartimento di Giurisprudenza
Università degli Studi di Bari

47°
BA
Congresso Nazionale
di **Chimica Inorganica**

PROCEEDINGS

Società Chimica Italiana
Divisione di Chimica Inorganica

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UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO
DIPARTIMENTO DI CHIMICA

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CONSIGLIO REGIONALE DELLA PUGLIA

47° Congresso Nazionale della Divisione di Chimica Inorganica

9-12 Settembre 2019, Bari

BOOK OF ABSTRACTS

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SUMMARY

Welcome

The University of Bari "Aldo Moro", Politecnico of Bari, Area della Ricerca of CNR and City of Bari are very pleased and honoured to host the **47th National Conference on Inorganic Chemistry from 9 to 12 September 2019**.

Today, Chemistry has a pivotal role both in basic and applied research and represents the connection bridge among scientific disciplines such as physic, biology, medicine and engineering. Its essence is well described by the **Periodic Table**, that is the scheme that has allowed sorting the chemical elements. It is well known that such Table marked and important step in the history of chemistry, thanks to which this science plays today a crucial role in seeking of solutions for global challenges.

To celebrate the importance of Periodic Table and the 150th anniversary of its introduction by Mendeleev, **UNESCO has proclaimed 2019 "International Year of the Periodic Table of Chemical Elements (IYPT2019)**".

Inorganic Chemistry deals with all chemical elements of Periodic Table and, thus, it has a leading role among chemistry sciences. Thanks to this branch of the Chemistry, several questions of basic research have today an answer and several solutions to problems of everyday life have been proposed.

The meeting, organized annually by the Inorganic Chemistry Division of the Italian Chemical Society, reaching the 47th edition in 2019 and, as is traditional, it will be one of the main events for researchers, teachers, students and people working in this sector.

On this basis, The City of Bari is very proud to host the 46th National Conference on Inorganic Chemistry.

We look forward to welcoming you!

The Organizing Committee

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-

Scientific Program

Monday 9 September 2019

University of Bari "Aldo Moro" Piazza C. Battisti 1

12:00 – 14:30	***Registration***	
14:30 – 14:45	***Opening*** **(Aula Magna "Aldo Moro")**	
	Aula Magna "Aldo Moro" **Chair: Emma Gallo**	
14:45 – 15:30	**PL1 Plenary Lecture**: **Thomas R. Ward** University of Basel, Basel (Swizerland) *Artificial Metalloenzymes: Challenges and Opportunities*	
15:30 – 16:00	**KN1 Keynote Lecture: Sander Leeuwenburgh** Radboud University, Nijmegen (The Netherlands) *Regeneration of diseased bone by local delivery of therapeutic biomolecules from organic-inorganic composite biomaterials*	
16:00 – 16:30	***Coffee break***	
	Aula Magna "Aldo Moro" **Chair: Tiziana Marino**	**Aula "Vincenzo Starace"** **Chair: Mario Chiesa**
16:30 – 16:45	**O1 Michele Benedetti** Università del Salento, Lecce (Italy) *Is hydrogen electronegativity higher than Pauling's value? New clues from the* ^{13}*C and* ^{29}*Si NMR chemical shifts of [AHF*$_3$*] (A = C, Si) compounds*	**O2 Andrea Biffis** Università di Padova, Padova (Italy) *Direct Alkyne Hydroarylation Catalyzed by Late Transition Metals: Mechanistic Insights and Improved Performance in Ionic Liquids*
16:45 – 17:00	**O3 Fabio Carniato** Università del Piemonte Orientale, Alessandria (Italy) *Mn(II) picolinates complexes as potential MRI probes*	**O4 Giorgio Volpi** Università di Torino, Torino (Italy) *New blue fluorescent Zinc(II) complexes with high quantum yield based on tuneable 1,3-substituted-imidazo[1,5-a]pyridine ligands*
17:00 – 17:15	**O5 Maria I. Nardella** Università degli Studi di Bari, Bari (Italy) *Interplay between zinc and copper binding to metallochaperone Atox1 and the N-terminal domain of Menkes ATPase*	**O6 Roberto Gobetto** Università di Torino, Torino (Italy) *M(bpy-R)(CO)*$_3$*X (M=Mn, X=Br or M=Re, X=Cl) catalysts for homogeneous and heterogeneous CO*$_2$ *electroreduction*
17:15 – 17:30	**O7 Tiziano Marzo** Università di Pisa, Pisa (Italy) *Human Serum Albumin and Cisplatin, a Still Ongoing Debate*	**O8 Daniela Intrieri** Università degli Studi di Milano, Milano (Italy) *Porphyrin-based systems: homogeneous catalysts for the CO*$_2$ *cycloaddition to epoxides and aziridines*
17:30 – 17:45	**O9 Michele Iafisco** CNR, Faenza (Italy) *Inhalable Calcium Phosphate Nanoparticles for Cardiac Drug Delivery*	**O10 Angela Dibenedetto** Università di Bari, Bari (Italy) *Selective catalysts driven polyols oxidation in sustainable conditions*

17:45 – 18:00	**O11 Mario Prejano** Università della Calabria, Rende (Italy) *From natural enzymes to synthetized catalyst: the nitrile hydration. Insights from theory.*	**O12 Walter Baratta** Università di Udine, Udine (Italy) *Catalytic C-H Activation Reactions Catalyzed by Monocarbonyl Ruthenium Complexes*
18:00 – 18:15	**O13 Benny D. Belviso** CNR, Bari (Italy) *How platinum anticancer drugs affect Atox1 and copper ion interaction: a crystallographic investigation*	**O14 Giovanni Pamparano** Università di Genova, Genova (Italy) *Ethanol conversion over copper based catalytic systems.*
18:30 – 20:00	***Welcome Party (PALACE CAFÈ Bari)***	

Tuesday 10 September 2019

University of Bari "Aldo Moro" Piazza C. Battisti 1

	Aula Magna "Aldo Moro" **Chair: Francesco P Fanizzi**	
9:00 – 9:45	**PL2 Luigi Sacconi Medal 2019: Liberato Manna** Istituto Italiano di Tecnologia (IIT) Genova (Italy) *Halide Perovskite Nanocrystals: Their Synthesis, Chemical, Structural, and Surface Transformations*	
9:45 – 10:15	**KN2 Keynote Lecture: Fabio Biscarini** Università degli Studi di Modena e Reggio Emilia, Modena (Italy) *Neuromorphic electronics biosensors*	
10:15 – 10:45	***Coffee break***	
	Aula Magna "Aldo Moro" **Chair: Tiziana Marino**	**Aula "Vincenzo Starace"** **Chair: Alberto Credi**
10:45 – 11:00	**O15 Francesco Bellia** CNR, Catania (Italy) *Reactive carbonyl species and copper(II) as competitive effectors of α-Synuclein*	**O16 Giuseppe Valerio Bianco** CNR, Bari (Italy) *Chemical Vapor Deposition of 2D Materials*
11:00 – 11:15	**O17 Daniela Lalli** Università del Piemonte Orientale, Alessandria (Italy) *Solution and solid-state NMR study of saponite clays intercalated with paramagnetic chelates*	**O18 Diego Colombara** Università degli Studi di Genova, Genova (Italy) *Point Defect Formation via Reactions at Chalcogenide Surfaces*
11:15 – 11:30	**O19 Damiano Cirri** Università di Firenze, Firenze (Italy) *Labelling metallodrug candidates with fluorescent dyes: some relevant examples*	**O20 Marcello La Rosa** Università di Bologna, Bologna (Italy) *The reversible electronic energy transfer in quantum dots-based inorganic-organic nanohybrids*
11:30 – 11:45	**O21 Erika Ferrari** Università di Modena, Modena (Italy) *Novel Curcumin-based radiotracers for Gallium-68 and Scandium-44*	**O22 Lorenzo Tesi** Università degli Studi di Firenze, Firenze (Italy) *Multitechnique Investigation for Rational Design of Molecular Spin Quantum Bits*
11:45 – 12:00	**O23 Marilena Carbone** Università di Roma Tor Vergata, Roma (Italy) *Unrevealing the real pigment composition of green tattoo inks*	**O24 Mariangela Oggianu** Università di Cagliari, Cagliari (Italy) *Optical sensing of heavy metal ions by sol-gel based plasmonic nanostructures*
12:00 – 12:15	**O25 Eloisa Sardella** CNR, Bari (Italy) *Plasma Activated Liquid Media as new pharmacological formulations to exacerbate cell oxidative stress*	**O26 Nicolas Godbert** Università della Calabria, Rende (Italy) *Self-Assembling in Water Soluble Ir(III) Complexes: From Hydrogels to Nanostructured IrO_2 Thin Films*

12:15 – 12:30	**O27 Daniele A. Cauzzi** Università di Parma, Parma (Italy) *The coordination chemistry of a unique zwitterionic ligand*	**O28 Maria M Natile** CNR, Padova (Italy) *NIR-light-driven generation of reactive oxygen species using Ru(II)-decorated phospholipid-coated upconverting nanoparticles*
12:30 – 14:00	***Lunch***	
	Aula Magna "Aldo Moro" **Chair: Giovanni Natile**	
14:00 – 14:45	**PL3 Plenary Lecture**: Winner of Nasini Prize, **Alessia Colombo** Università degli Studi di Milano, Milano (Italy) *Coupling of a Copper Dye with a Copper Electrolyte: the Birth of Sustainable "Full-Copper" Dye-Sensitized Solar Cells*	
14:45 – 15:15	**KN3 Keynote Lecture: Michele Melchionna** Università degli Studi di Trieste, Trieste (Italy) *Chasing the nanocarbon in the wonderland of sustainable catalysis*	
	Aula Magna "Aldo Moro" (Premi Dottorato 2019) **Chair: Michele Aresta**	
15:15 – 15:30	**O29** Winner of the PhD Prize: **Davide Corinti** Dipartimento di Chimica e Tecnologie del Farmaco, Università di Roma "La Sapienza", Roma (Italy) *Reaching a new level of understanding of the bioinorganic chemistry of Pt drugs using MS-based techniques*	
15:30 – 15:45	**O30** Winner of the PhD Prize: **Riccardo Freccero** Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Genova (Italy) *Study of new polar intermetallic compounds: synthesis, structural relations and real space chemical bonding analysis*	
15:45 – 16:00	**O31** Winner of the PhD Prize: **Gabriel Menendez Rodriguez** Department of Chemistry, Biology and Biotechnology, University of Perugia and CIRCC (Italy) *Organometallic Iridium Complexes as Efficient Catalysts for Renewable Energy Applications*	
16:00 – 16:30	***Coffee break***	
	Aula Magna "Aldo Moro" **Chair: Francesco Fracassi**	**Aula "Vincenzo Starace"** **Chair: Carlo Mealli**

16:30 – 16:45	**O32 Lidia Armelao** Università di Padova, Padova (Italy) *UV and X-ray Excited Optical Luminescence in* Cr^{3+} *doped* $ZnGa_2O_4$ *thin films: a case study*	**O33 Emanuele Priola** Università di Torino, Torino (Italy) *Bridging Solution and Solid-State Chemistry of Dicyanoaurate: The Case Study of Zn-Au Nucleation Units*
16:45 – 17:00	**O34 Diaa Aref** Università di Napoli "Federico II", Napoli (Italy) *Synthesis and characterization of a new class of Ru-based photosensitizer*	**O35 Rocco Caliandro** CNR, Bari (Italy) *Structural characterization of halide perovskites by X-ray measurements and advanced analysis*
17:00 – 18:00	***Poster session***	
18:00 – 19:30	***Divisional Assembly***	

Wednesday 11 September 2019

University of Bari “Aldo Moro” Piazza C. Battisti 1

	Aula Magna “Aldo Moro” **Chair: Adriana Saccone**	
9:00 – 9:45	**PL4 Paolo Chini Memorial Lecture: Rinaldo Poli** Université de Toulouse, Toulouse (France) *Homolytically weak metal-carbon bonds and the persistent radical effect in metal-mediated radical polymerization*	
9:45 – 10:15	**KN4 Keynote Lecture: Petrus Henricus Maria Budzelaar** Università degli Studi di Napoli “Federico II” Napoli (Italy) *Innocent and Less Innocent Ligands*	
10:15 – 10:45	***Coffee break***	
	Aula Magna “Aldo Moro” **Chair: Francesco Fracassi**	**Aula “Vincenzo Starace”** **Chair: Emma Gallo**
10:45 – 11:00	**O36 Gigliola Lusvardi** Università di Modena, Modena (Italy) *Mesoporous bioactive glasses doped with cerium investigation over enzymatic-like mimetic activities and bioactivity*	**O37 Jacopo Andreo** Università di Parma, Parma (Italy) *Zwitterionic Metallates of HEtSNS: Synthesis and Characterization of Bis- and Tris-Chelated Coordination Compounds*
11:00 – 11:15	**O38 Stefano Cattaneo** Università degli Studi di Milano, Milano (Italy) *Carbonaceous materials for the selective hydrogenation of HMF*	**O39 Alessandro Motta** Università di Roma La Sapienza, Roma (Italy) *Theoretical Insights on a biocompatible reduction route of graphene oxide by N-acetyl cysteine*
11:15 – 11:30	**O40 Gabriele Manca** CNR, Sesto Fiorentino (Italy) *Electronic/Structural Aspects of the Functionalization of Phosphorene*	**O41 Fiorenza Fanelli** CNR, Bari (Italy) *Atmospheric pressure plasma processing of polyurethane sponges for oil-water separation*
11:30 – 11:45	**O42 Giorgio Facchetti** Università degli Studi di Milano, Milano (Italy) *A new artificial reductase based on the D-Ala-D-Ala/Vancomycin supramolecular interaction and its applications in the enantioselective reduction of cyclic imines*	**O43 Mariachiara Trapani** CNR, Messina (Italy) *Inorganic nanostructured templates for porphyrin J aggregates growth*
11:45 – 12:00	**O44 Ambra Maria Fiore** Politecnico di Bari, Bari (Italy) *Synthesis, characterization and catalytic applications of transition metal nanoparticles-based embedded in polymeric nanoreactors.*	**O45 Enrico Salvadori** Università di Torino, Torino (Italy) *Nature and Topology of Metal-Oxygen Binding Sites in Zeolite Materials*
12:00 – 12:15	**O46 Claudio Garino** Università di Torino, Torino (Italy) *Light-activated Generation of NO and SO_3^- from a Ruthenium Nitrosylsulfito Complex*	**O47 Chiara Parise** Università di Bologna, Bologna (Italy) *Supported gold nanoparticles catalysts for organic transformations*

12:15 – 12:30	**O48 Elisa Moretti** Università di Venezia, Venezia (Italy) *Flower-like Ce-Ti oxide systems for the CO preferential oxidation under solar light irradiation*	**O49 Sofia Capelli** Università di Milano, Milano (Italy) *Influence of Pd NPs size for bio-adipic acid production from muconic acid and sodium muconate*
12:30 – 14:00	***Lunch***	
	Aula Magna "Aldo Moro" **Chair: Alceo Macchioni**	
14:00 – 14:45	**PL5 Plenary Lecture**: **Massimiliano Delferro** Argonne National Laboratory USA *Catalysis and Inorganic Chemistry at U.S. DOE Argonne National Laboratory*	
14:45 – 15:15	**KN5 Keynote Lecture: Salvatore Sortino** Università degli Studi di Catania, Catania (Italy) *Light-Triggered Activation and Synthesis of Hybrid Nanoconstructs for Biomedical Applications*	
	Aula Magna "Aldo Moro" **Chair: Michele Saviano**	**Aula "Vincenzo Starace"** **Chair: Mario Chiesa**
15:15 – 15:30	**O50 Daniela Marasco** Università di Napoli Federico II, Napoli (Italy) *Inhibition of amyloid aggregation by transition metal complexes*	**O51 Fabio Palumbo** Università di Bari, Bari (Italy) *Plasma-assisted deposition of fungicide containing coatings for encapsulation and protection of maize seeds*
15:30 – 15:45	**O52 Francesco Attanasio** CNR, Catania (Italy) *Carnosine and trehalose-carnosine interplay in the activation of CREB functions and copper homeostasis*	**O53 Francesco Giannici** Università di Palermo, Palermo (Italy) *Assessing the Electrode-Electrolyte Compatibility in Solid-Oxide Cells with X-ray Microspectroscopy*
15:45 – 16:00	**O54 Diego Lamendola** Università di Pisa, Pisa (Italy) *Angiogenin bound to gold nanoparticles induces wound healing in the presence of copper ions*	**O55 Antonella Milella** Università di Bari, Bari (Italy) *Plasma-assisted deposition of iron oxide thin films as photoanodes for water splitting*
16:00 – 16:30	***Coffee break***	
16:30 – 17:30	***Poster session***	
17:30 – 19:30	**Tavola Rotonda "La Tabella periodica e Primo Levi"** (evento aperto agli insegnanti, scuole e alla cittadinanza) coordina **Pietro Greco** Chimico, Divulgatore, Giornalista Scientifico partecipano Prof **Michele Aresta** e Prof **Giovanni Natile**	
20:00 – end	***Social Dinner (Palace Hotel Bari TERRAZZA MURAT)***	

Thursday 12 September 2019

University of Bari "Aldo Moro" Piazza C. Battisti 1

	Aula Magna "Aldo Moro" **Chair: Francesco P. Fanizzi**	
9:00 – 9:45	**PL6 Plenary Lecture**: **Clotilde Policar** École Normale Supérieure, Paris (France) *Metal complexes in biology: a new frontier in inorganic chemistry*	
9:45 – 10:15	**KN6 Keynote Lecture: Emilia Sicilia** Università della Calabria Arcavacata di Rende, Cosenza (Italy) Mechanism of action of metal-containing anticancer drugs. Insights from computations	
10:15 – 10:45	***Coffee break***	
	Aula Magna "Aldo Moro" **Chair: Michele Saviano**	**Aula "Vincenzo Starace"** **Chair: Alceo Macchioni**
10:45 – 11:00	**O56 Marta Erminia Alberto** *Università della Calabria, Rende (Italy)* *Dual-approach PtII-BODIPY conjugates: Theoretical Insights*	**O57 Francesco Nocito** Università degli Studi di Bari, Bari (Italy) *Valorization of C5 polyols by direct carboxylation to FDCA: synthesis and characterization of a key intermediate and role of carbon dioxide*
11:00 – 11:15	**O58 Gaetano Malgieri** Università della Campania, Caserta (Italy) *Metal ion recruitment drives the folding mechanism and self-association propensity of high homologous proteins*	**O59 Cristina Tubaro** Università di Padova, Padova (Italy) *Novel heterobimetallic complexes by coordination of nNHC/tzNHC heteroditopic carbene ligands*
11:15 – 11:30	**O60 Nazareno Re** Università di Chieti, Pescara (Italy) *Multiscale Modeling of the Au(I) Chelating Motif in Protein golB*	**O61 Andrea Ienco** CNR, Sesto Fiorentino (Italy) *Towards a Definition of Metal Organic NanoTube (MONT)*
11:30 – 11:45	**O62 Mauro Ravera** Università del Piemonte Orientale, Alessandria (Italy) *In vitro and In vivo Properties of Pt(IV) Bifunctional Prodrugs Containing the 2-(2-Propynyl)octanoato Axial Ligand*	**O63 Alice De Paolo** Università di Pisa, Pisa (Italy) *Synthesis and investigation of new iridium complexes containing tetramethylcyclopentadienyl ligands variably substituted as potential catalysts for water oxidation*
11:45 – 12:00	**O64 Denise Lovison** Università di Udine, Udine (Italy) *Chiral ruthenium complexes: synthesis and evaluation of their anticancer activity*	**O65 Federico Nicoli** Università di Bologna, Bologna (Italy) *Ethereal Love: promoting ring-to-ring interaction in a [3]Rotaxane*
12:00 – 12:15	**O66 Alessandra Barbanente** Università degli Studi di Bari, Bari (Italy) *Platinum-loaded, Selenium-doped hydroxyapatite for potential applications in bone tumors therapy*	**O67 Francesca Tessore** Università di Milano, Milano (Italy) *Electronic Properties of Electron-Deficient Zn(II) Porphyrins for HBr Splitting*
12:15 – 12:30	***Final Event***	
12:30 – 12:45	***Award Ceremonies***	
12:45 – 13:00	***Closing***	

Plenary Conferences

PL1 Artificial Metalloenzymes: Challenges and Opportunities

Thomas Ward [a]

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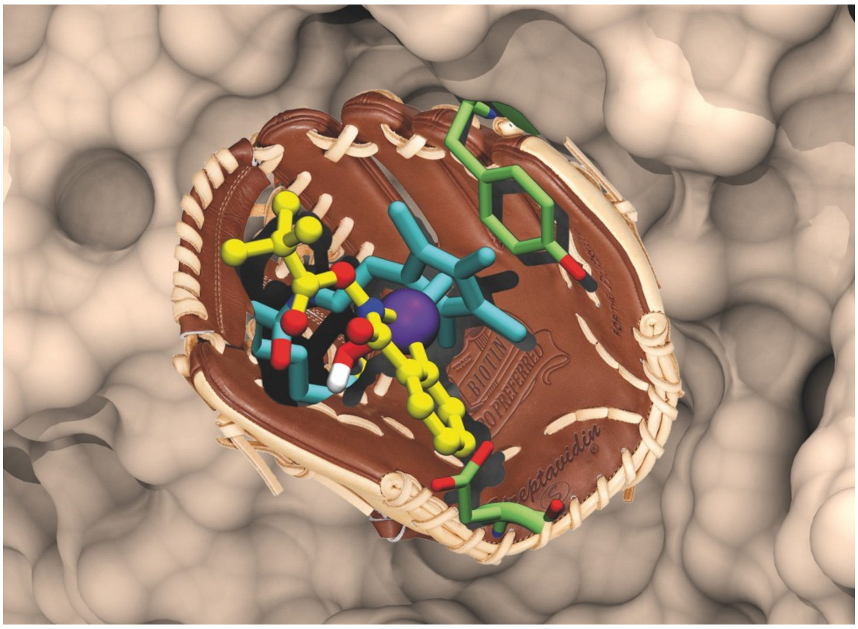
Artificial metalloenzymes (ArMs) result from the incorportation of a catalyst precursor within a host protein, see Scheme. The resulting hybrid catalysts display features that are reminiscent of both homogeneous catalysts and enzymes, Figure 1. The optimization of the catalytic performance of ArMs is achieved by combining both chemical- and genetic means. The versatility of this chemo-genetic optimization strategy will be illustrated with selected examples including: transfer-hydrogenation, C–H activation, olefin metathesis, hydroamination etc.

With the aim of integrating artificial metalloenzymes *in vivo*, the second part of the talk will present our efforts to combine ArMs with natural enzymes to mimic essential features of the metabolism including: cascade reactions as well as up- and cross- regulation. Having identified the critical metabolites leading to ArM's inhibition, our efforts towards engineering enzyme cascades *in vivo* will be summarized.



Reaction implemented
Hydrogenation
Transfer hydrogenation
Hydroamination Allylic substitution Suzuki cross-coupling Dihydroxylation
Sulfoxidation
Alcohol oxidation
Peroxidation Olefin metathesis C–H activation
Cyclopropanation Michael addition Enzyme cascades

***Figure 1**: Anchoring a catalyst precursor (ball & stick representation) within a host protein (baseball glove) affords an artificial metalloenzyme. The catalytic performance of the resulting hybrid catalyst can be optimized by chemo-genetic means: variation of the nature and position of the cofactor (turquoise stick representation) and mutation of aminoacid residues (green stick representation).*

PL2 Halide Perovskite Nanocrystals: Their Synthesis, Chemical, Structural, and Surface Transformations

Liberato Manna[a]

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Halide perovskite semiconductors can merge the highly efficient operational principles of conventional inorganic semiconductors with the low-temperature solution processability of emerging organic and hybrid materials, offering a promising route towards cheaply generating electricity as well as light. Perovskites not only show exceptional primary optoelectronic properties such as a direct bandgap, small exciton binding energy, low carrier recombination rates, ambipolar transport, and tunability of the bandgap covering a wavelength range from the near-infrared to the ultraviolet, but they are also very attractive for their ease of processability for mass production (e.g. printing from solution) and for the large availability of their chemical components. Following a surge of interest in this class of materials, research on halide perovskite nanocrystals as well has gathered momentum in the last years. In such a narrow time span, several properties/features of halide perovskite nanocrystals were investigated, among them electroluminescence, lasing, anion-exchange, as well as control of size and shape [1-2]. Important developments include doping, synthesis of Pb-free perovskite nanocrystals, and investigations of their rich surface chemistry, combining a variety of experimental techniques and computational approaches. The present talk will highlight the research activities of our group on halide perovskite and perovskite-related nanocrystals, with emphasis on synthesis, as well as structural, chemical, and surface transformations, and applications in devices [3]. Especially the surface chemistry of these nanocrystals makes them susceptible to degradation and long-term instability, and the surface can introduce mid-gap trap stated. Thus, careful engineering of the interface between the perovskite nanocrystals and the organic ligands is fundamental to improve device performance and long term stability [4].

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[1] Q. A. Akkerman, G. Rainò, M. Kovalenko and L. Manna, *Nat Mater.* **2018**, 17, 394-405.

[2] J. Shamsi, A. S. Urban, M. Imran, L. De Trizio, and L. Manna, *Chem. Rev.* **2019**, 119, 3296–3348.

[3] Q. A Akkerman, M. Gandini, F. Di Stasio, P. Rastogi, F. Palazon, G. Bertoni, J. M. Ball, M. Prato, A. Petrozza, and L. Manna, *Nat. Energy* **2017**, 2, 16194.

[4] G. Almeida, I. Infante, and L. Manna, *Science* **2019**, doi:10.1126/science.aax5825.

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PL3 Coupling of a Copper Dye with a Copper Electrolyte: the Birth of Sustainable “Full-Copper” Dye-Sensitized Solar Cells

Alessia Colombo[a]

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To have enough clean and low cost energy for the future is one of the world’s most important challenges. Since the discovery of Grätzel-type dye-sensitized solar cells (DSSCs) as a convenient way for harnessing the energy of the sun and converting it into electricity, there has been a lot of effort to improve the photo-conversion efficiency, trying to optimize the sensitizer and the redox mediators. Until recently, the most efficient DSSCs were based on ruthenium complexes as dye and the iodide/triiodide couple as redox mediator. However, ruthenium is one of the rarest and most expensive metal, and this is a drawback in the design of low-cost DSSCs. Photophysical, economic, and environmental considerations make copper(I) coordination compounds interesting alternatives to ruthenium dyes [1-2]. Besides, it was found that Cu-based mediators can outperform both iodine-based and Co-based electrolytes [2]. These observations were the springboard for the first “full-copper” DSSCs in which a copper(I) dye is coupled with a copper(I)/(II) electron shuttle, of great interest for the development of novel low cost and environmentally friendly DSSCs.

This presentation is on the birth of “full-copper” DSSCs. First, it will be shown how homoleptic and heteroleptic copper(I) dyes can be coupled with the common I^-/I_3^- redox couple to prepare DSSCs with a good efficiency. Then, some examples of the use of homoleptic Cu(I)/(II) mediators, in combination with both ruthenium(II) dyes and organic dyes, will be given. Finally, the coupling of a copper dye with a copper electrolyte as a fascinating route for sustainable “full-copper” DSSCs will be presented.

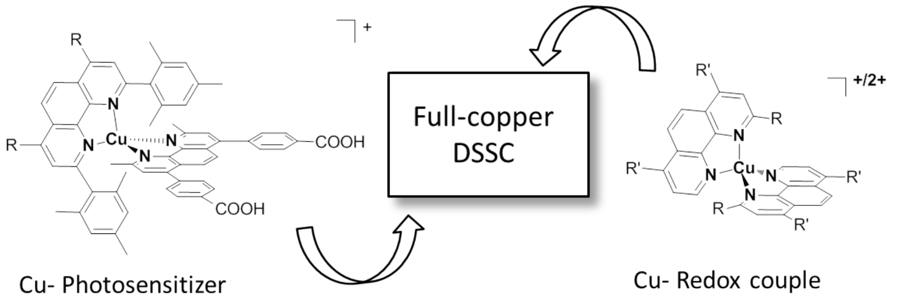

***Figure 1**: general structure of the involved copper complexes*

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PL4 Homolytically weak metal-carbon bonds and the persistent radical effect in metal-mediated radical polymerization

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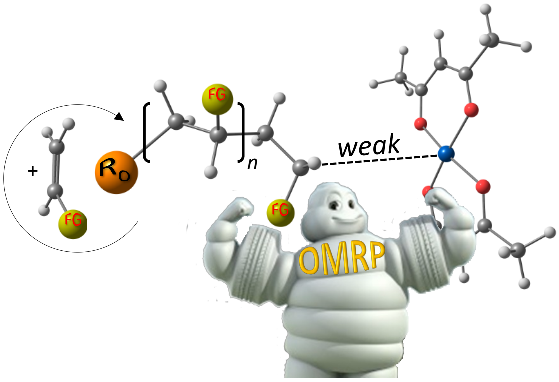

Transition metal alkyl complexes are the quintessence of organometallic chemistry. Their high reactivity often requires strictly controlled conditions for their synthesis and study, but this reactivity (e.g. reductive elimination, insertion, etc.) can be harvested to accomplish many useful catalysed processes. Homolytic cleavage of the metal-carbon bond is another possible decomposition pathway of organometallic compounds, thus most investigated systems feature sufficiently strong bonds. However, homolytic bond cleavage to produce carbon-based radicals can also be harvested, via the principle of the "persistent radical effect" (PRE),[1] to accomplish useful chemical processes such as selective transformations in metal-mediated organic synthesis[2] and controlled radical polymerization.[3] Specifically, there has been an explosion of research activity in the polymer area after the discovery of various methods to insure pseudo-living chain growth and to engineer elaborate, high-added-value polymeric architectures. Transition metal complexes may serve as moderating species, as in Atom Transfer Radical Polymerization (ATRP) and Organometallic Mediated Radical Polymerization (OMRP). This lecture will illustrate how the accurate calculation,[4] backed up by experimental benchmarking,[5] of homolytic metal-carbon bond dissociation energies has permitted to achieve unprecedented control for the radical polymerization of challenging monomers such as vinyl acetate[6] and vinylidene fluoride.[7]

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PL5 Catalysis and Inorganic Chemistry at U.S. DOE Argonne National Laboratory

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Systematic study of the interactions between organometallic catalysts and metal oxide support materials is essential for the realization of rational design in heterogeneous catalysis. In this talk, I will first describe the stoichiometric and catalytic chemistry of a series of organometallic complex chemisorbed on a variety of metal oxides as a multifaceted probe for stereoelectronic communication between the support and organometallic center. Electrophilic bond activation was explored in the context of stoichiometric hydrogenolysis as well as catalytic hydrogenation, dehydrogenation, and H/D exchange. Strongly acidic modified metal oxides such as sulfated zirconia engender high levels of activity toward electrophilic bond activation of both sp^2 and sp^3 C–H bonds, including the rapid activation of methane at room temperature; however, the global trend for the supports studied here does not suggest a direct correlation between activity and surface Brønsted acidity, and more complex metal surface interactions are at play.[1, 2, 3, 4]

In a second example of catalysis at Argonne National Laboratory, I will present the development of efficient and innovative catalytic inorganic materials for converting waste polymers into more valuable products in a selective manner – catalytic upcycling. Synthetic polymers are ubiquitous and critical to the function of modern life. However, the ubiquity of polymers has resulted in an enormous and growing amount of polymer waste, which has a long lifetime in the environment and is inefficient to recycle. Polymer waste is both a threat to the environment and economy, and an untapped resource of energy-rich hydrocarbons. If the large macromolecules that make polymers could be chemically transformed or "upcycled" into value-added chemicals, rather than disposed of as waste or downcycled into lower grade plastics, the energy and value put into the polymers could be reclaimed and turned into new applications.

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Acknowledgements: *This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract DE-AC02-06CH11357.*

PL6 Metal complexes in biology: a new frontier in inorganic chemistry

Focuses on Mn-SOD mimics and X-fluorescence imaging

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Metal complexes are increasingly used for biological applications, as metal-centered probes for imaging or as metal-based drugs.[1, 2] To be active a metal complex must reach its biological target that can be buried in cells. Intracellular quantification, speciation of the metal cation, and intracellular distribution through imaging, as well as the evaluation of the activity directly in a cellular environment are key steps in the design and study of metallo-active bio-molecules.

In this talk, we will show how cellular models can be designed to evaluate the activity of metal-based anti-oxidants mimicking the anti-oxidant and cell-protective proteins, superoxide dismutases (SOD). Such Mn-complexes reproducing the activity of SOD are called SOD-mimics. Most of the metal complexes studied in the literature for their bio-activity are used as anti-cancer or anti-bacterial agents, and, because of that, most of the corresponding bio-analyses are focusing on toxic effects. In contrast, anti-oxidants and SOD mimics are meant to restore normal functioning of cells by limiting oxidative stress. Specific non-routine strategies are thus required to characterize their bio-activity.[3-5] Imaging is also key to the full understanding of the bio-properties of any drug and specific techniques can be used to image these metallo-drugs. Other applications of imaging using metal-metal-based probes will also be presented. More specifically, probes made of a central metal-CO core, called SCoMPIs (for single core multimodal probes for imaging), can be mapped using unconventional imaging techniques such as IR and X-fluorescence imaging.[6-8]

These topics have been chosen to exemplify a range of approaches at this new frontier in inorganic chemistry.

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Keynote Lectures

KN1 Regeneration of diseased bone by local delivery of therapeutic biomolecules from organic-inorganic composite biomaterials

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Bioceramics such as calcium phosphates and bioactive glasses are frequently used to stimulate the regeneration of bone tissue due to their superior compatibility with bone tissue. Nevertheless, these bioceramics are still associated with several drawbacks such as their inherent brittleness, poor clinical handling behavior and limited biological activity. Therefore, bioceramics have been combined with organic biomaterials for several decades. Since the 1990s, the emergence of nanotechnology has accelerated the development of organic-inorganic nanocomposites which exhibit improved functionality and therapeutic efficacy as compared to conventional composite biomaterials.

This presentation will highlight recent developments in biomaterials research focusing on the design of novel organic-inorganic composite biomaterials for regeneration of bone suffering from degenerative diseases such as osteoporosis, infection or bone cancer. Innovative approaches will be presented which facilitate local delivery of therapeutic biomolecules from injectable organic-inorganic composite biomaterials containing biomolecule-loaded nanocarriers. Specific attention will be paid to local delivery of antibiotics (vancomycin), anti-osteoporotic drugs (bisphosphonates) and anticancer drugs (platinum-based complexes). The presented data open up new avenues of research on the application of novel organic-inorganic biomaterials for treatment of diseased bone.

KN2 Neuromorphic electronics biosensors

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Organic electronics devices are emerging as ultra-sensitive and specific biosensors. Electrolyte gated organic field effect transistors (EGOFET) and organic electrochemical transistors (OECT) are the most used architectures. According to the current understanding two different doping mechanisms intervene in these devices: EGOFET operate in accumulation due to electrostatic doping of ions at the electrical double layer at the interface between the organic semiconductor and the electrolyte; OECT operate in depletion by electrochemical doping upon gate-modulated cation exchange. I will discuss here a unified view of ion-gating mechanism in the two architectures by means of a common mechanism that is based on ion-pi conjugated molecule interaction, a strong non-covalent interaction that is widely studied in protein chemistry and ion batteries, but still overlooked in organic electronics. The shift of HOMO-LUMO levels in the pi-materials indicate that that the ions can modulate the hopping rate of the charge carriers, and specifically for p-type materials, cations will slow down producing a lower conductivity, while anions will accelerate it, thus increasing the current. This scenario also hints to the fact that the "bulk" of an organic semiconductor thin film is involved in the modulation of the charge transport in EGOFET, similarly to the mechanism invoked in OECT. These concepts have inspired us to design a new sensor for dopamine (DA), which can be ultra-sensitive and specific at the same time. The sensing device is operated in frequency as a “synapse-like transistor”, either in a two terminal or a three-terminal device. Synapstors can be fabricated with hybrid organic/nanoparticle active layers, else whole organic. The characteristic time scale of the synapstor is used as the signal correlate to the concentration. DA levels in the brain of healthy people are in the nanomolar range of concentration and decrease to 100-picomolar range in patients with Parkinson’s disease (PD). The selectivity of the sensor was also tested in operational conditions nearer to the *in vivo* ones in co-presence of physiological concentration of ascorbic acid and uric acid. We also assessed the sensor against the whole series of DA catabolites, showing the capability of the sensor to discriminate sub-molecular changes of the chemical structure, or non-covalent interactions. Once properly engineered, the proposed sensor could be coupled with actuating devices, leading to the implementation of implantable architectures for the Central Nervous System, that may perform loco-regional delivery of L-Dopa in response to [DA] lowering in animal models, and later in patients, affected by Parkinson’s disease. This work is supported by UNIMORE FAR 2015 Project “PRODE”, FAR 2018 Project “E-MAP”, and EuroNanoMed III Project “AMI”.

KN3 Chasing the nanocarbon in the wonderland of sustainable catalysis

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The role of carbon nanostructures in heterogeneous catalysis related to sustainable processes has been increasingly clarified over the last two decades.[1] Research efforts have focused on the importance of integrating nanocarbons in the formulation of carbon-inorganic nanohybrids catalysts with superior electro-catalytic features in crucial energy processes such as the reduction of CO_2 to carbon fuels[2] and the evolution of hydrogen from water,[3] as well as in the sustainable electro-synthesis of key industrial compounds such as hydrogen peroxide.[4] Moreover, nanocarbons have emerged as important components in enhancing activity of nanohybrid catalysts for hydrogen production, through photo-induced[5] or thermal processes.[6] This bulk of studies project the nanocarbons as versatile promoters or stabilizers in the assembly of materials for sustainable catalytic chemistry.

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KN4 Innocent and Less Innocent Ligands

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Diiminepyridine (DIP) ligands frequently display ligand-centred reactivity. We report on formation of formally low-valent Ti/Zr/Hf DIP complexes (studied earlier by Calderazzo[1]) and conclude that in most cases the ligand has undergone reduction.[2] In addition, we have observed spontaneous ligand isomerization to an amide/enamide form in several cases; odd-electron intermediates are likely to be involved.[3]

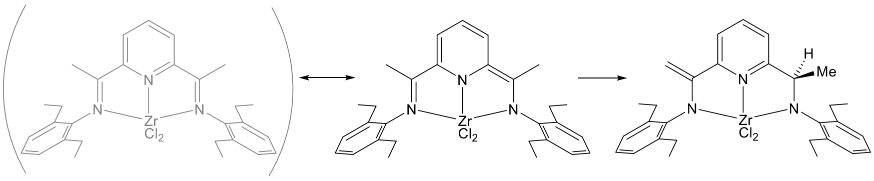

***Figure 1**: Bonding in and isomerization of (DIP)ZrCl$_2$*

On the other end of the scale, □-diiminate (BDI) ligands are mostly innocent and stabilize metals in low-coordinate environments. [(BDI)Rh]$_2$(□-Br)$_2$ is a true Rh(II) complex without a metal-metal bond. Reaction with a bulky lithium anilide produces a monomeric 13-*e* Rh(II) anilide with some Rh(I) aminyl character; with less hindered anilides C-H activation and C-N coupling are observed.[4]

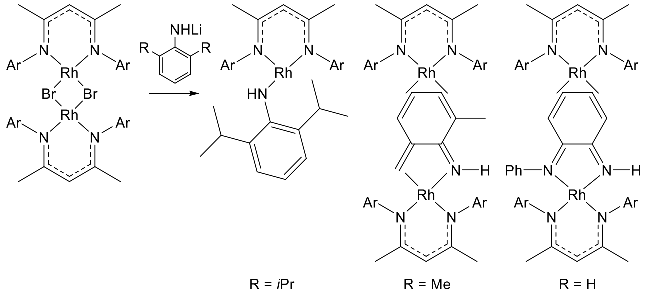

***Figure 2**: Reaction of [(BDI)Rh]$_2$(□-Br)$_2$ with Li anilides*

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KN5 Light-Triggered Activation and Synthesis of Hybrid Nanoconstructs for Biomedical Applications

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The achievement of nanoconstructs able to release single/multiple therapeutic species in a controlled fashion and to be tracked in a biological environment is a major challenge in the burgeoning field of nanomedicine.[1] Light is a powerful tool to fulfil these needs in a non-invasive way. By virtue of its easy manipulation in terms of energy, intensity, location and duration, light mimics an "optical syringe" that can activate fluorescence for imaging and stimulate a "burst" of therapeutics with superb spatiotemporal control, by using tailored photoresponsive nanomaterials.[2] Moreover light-triggering is bio-friendly and offers the additional advantages of not affecting important physiological parameters such as temperature, pH and ionic strength.

Besides its key role in the activation of therapeutic and imaging functionalities, photons represent powerful and "green" reactants for the facile synthesis of noble metal-based nanomaterials, which are suited for a variety of bio-applications due to their characteristic plasmonic absorption.

In our laboratories, we have been working on the design and fabrication of a number of hybrid nanoconstructs that can be activated, synthesized or both by using Visible/Near Infrared light as suitable trigger. This contribution illustrates some of the most recent examples at this regard, including mesoporous silica nanoparticles,[3-5] supramolecular nanoassemblies,[6] quantum dots[7] and differently shaped gold and silver nanostructures,[8,9] highlighting the rationale design and the potential relevance in biomedical research.

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KN6 Mechanism of action of metal-containing anticancer drugs. Insights from computations

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The rich chemistry of transition metal compounds allows to design anticancer therapeutic agents possessing pharmacokinetic properties inaccessible to organic systems. Nevertheless, in spite of the great deal of efforts devoted to the design and synthesis of alternative cytotoxic agents, the inorganic complex cisplatin, *cis*-$[Pt(NH_3)_2(Cl)_2]$ continues to be the most used chemotherapeutic agent for fighting cancer. The mechanism of action of cisplatin and its FDA approved carboplatin and oxaliplatin analogues involves that two labile ligands can be displaced in the cytoplasm, allowing the formation of bifunctional intra- and inter-strand DNA crosslinks, mostly with guanine nucleobases. These crosslinks distort the DNA helix, causing proteins to signal for apoptosis. Aiming at developing more selective drugs with less toxic side effects and lower inherent or acquired resistance, new classes of platinum and non-platinum complexes, exhibiting promising anticancer activity and also different activation mechanisms, have been proposed as non-classical alternatives. Here the outcomes of the computational investigations, carried out using DFT, of the mechanism of action of several examples of non-classical metal-containing cytotoxic agents, such as Pt(IV) prodrugs, monofunctional Pt(II) complexes, organoiridium(III) complexes, are illustrated.

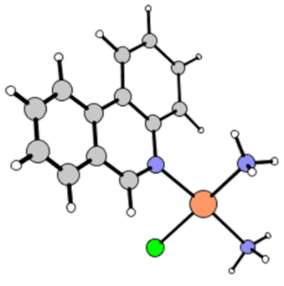

***Figure 1**: Phenanthriplatin monofunctional Pt(II) complex*

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Oral Presentations

O1 Is hydrogen electronegativity higher than Pauling's value? New clues from the ^{13}C and ^{29}Si NMR chemical shifts of $[AHF_3]$ (A = C, Si) compounds

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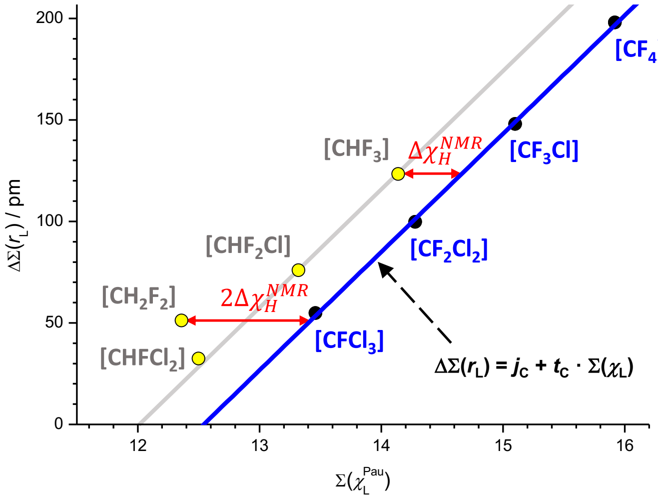
The study of the NMR chemical shift variations produced by monoatomic halido ligands bonded to NMR active central A atoms, in $[AX_n]$ compounds (X_n = combination of n halido ligands) is of wide interest. At this regard, we could previously demonstrate that the □ NMR chemical shift of a central ^{13}C or ^{29}Si atom, in simple $[AX_4]$ (A = C, Si; X_4 = combination of four halides) tetrahalido derivatives, can be directly related to both ionic radii and Pauling's electronegativities overall sums of the coordinated atomic ligands, $\sum(r_L)$ and $\sum(\chi_L^{Pau})$, respectively. [1,2] In this work, we extended this approach to halomethane and halosilane derivatives of the type $[AH_mX_n]$ (A = C, Si; X_n = combination of n halido ligands; n+m = 4), by studying the ^{13}C and ^{29}Si NMR chemical shift variations of $[AH_mX_n]$ compounds, as a function of $\sum(r_L)$ and $\sum(\chi_L^{Pau})$. In this way, new measurements for the hydrogen electronegativity, based on experimental molecular NMR data (χ_H^{NMR}), could be obtained. Remarkably, the hydrogen electronegativity obtained by these NMR data resulted higher than that reported by Pauling in its scale, but similar to that reported by Mulliken ($\chi_H^{NMR} = 2.75$; $\chi_H^{Pau} = 2.20$; $\chi_H^{Mulliken} = 2.80$). The importance of this new finding derives from the use of NMR data, based on molecular rather than atomic properties, in order to obtain a hydrogen electronegativity value similar to that calculated by Mulliken.

__Figure__: $\Delta\sum(r_L)$ differences vs. $\sum(\chi_L^{Pau})$ for = combination of four halido ligands) and hydrogenated $[CHX_3]$ (X_3 = combination of 3 halido ligands) for compounds with $\sum(\chi_L^{Pau}) > 12.4$. The parallel lines interpolating $[CX_4]$ and data (blue and grey, respectively) are $\Delta\chi_H^{NMR}$. This value accounts for the difference Pauling's and here calculated Hydrogen electronegativity ($\chi_H^{NMR} = 2.75$). Consistently $\Delta\chi_H^{NMR}$ doubles in the case of $[CH_2F_2]$.



$[CX_4]$ (X_4
mono

$[CHX_3]$
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O2 Direct Alkyne Hydroarylation Catalyzed by Late Transition Metals: Mechanistic Insights and Improved Performance in Ionic Liquids

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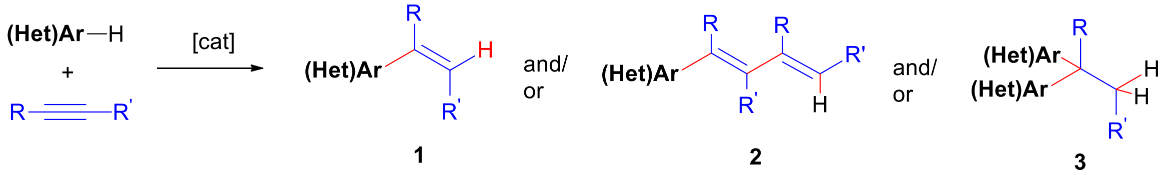
Among the numerous C-H bond functionalization reactions that have been disclosed and developed in recent years, the direct hydroarylation of alkynes shows great potential for practical applications, since it produces no waste and often exhibits a high, tunable and peculiar chemo-, regio- and stereoselectivity.[1]



Generally, in this reaction a C-H bond in an aromatic ring adds formally *trans* across the alkyne multiple bond, producing an alkenyl-substituted compound **1** with a Z configuration at the double bond. Depending on the nature of the reagents, the employed catalytic system and the reaction conditions, products of double alkyne insertion into the same arene C-H bond **2** may predominantly form.[2] We have now unravelled the mechanistic rationale for such a switch in chemoselectivity through a computational study, which has also shed new light on the role of the acid co-catalyst, which is generally employed in Pd-catalyzed reactions of this kind.

We have also extended the use of ionic liquids (ILs) as reaction media for hydroarylation reactions. We show here that combining ILs with Au-based catalytic systems very high activities under neutral conditions can be reached;[3] furthermore the reaction chemoselectivity between type **1** and **3** products can be controlled, acting in particular on the solubility of reagents and products in the IL. Such control enables *inter alia* the selective production of double C-H addition products by addition of two different heteroarenes to the same alkyne.

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O3 Mn(II) picolinates complexes as potential MRI probes

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Mn(II) shows several favourable magnetic properties and much better toxicity profile than the Gd^{3+} ion. For these reasons, Mn(II)-chelates can be considered a viable alternative to the Gd(III)-based MRI contrast agents currently used in clinics.[1] A considerable amount of Mn(II)-probes have been studied by the relaxometric point of view, aiming to determine the molecular parameters responsible of their MRI contrast efficiency (relaxivity). In this work, we investigated a pentadentate member of the picolinate family ($PAADA^{3-}$) for Mn(II) complexation and an amphiphilic derivative. The rotational correlation time (τ_R) and the electronic parameters of the Mn(II)-PAADA were extrapolated by the simultaneous best-fitting of the ^1H nuclear magnetic relaxation dispersion profiles (NMRD) and ^{17}O NMR relaxation and shift data.[2] The modification of the rotational dynamics was achieved through the functionalization of the pyridyl unit of the ligand with a lipophilic dodecyloxo group (Fig. 1). The functionalized chelate shows enhanced relaxivity compared to Mn(II)-PAADA, as a consequence of the reduced mobility of the complex in aqueous solution, and a high affinity with bovine serum albumin. The results reported here provide insight into important molecular parameters that control the efficiency of Mn^{2+} complexes as MRI contrast agents.

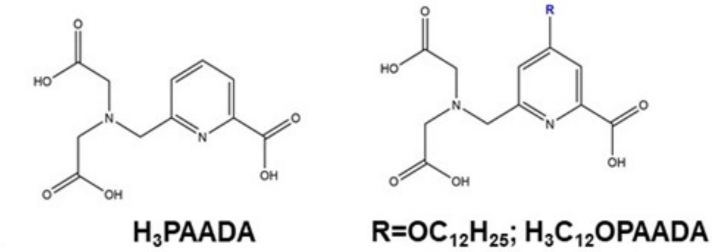

***Figure 1**: The structures of the ligands used for the preparation of the corresponding Mn^{2+}-chelates.*

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Acknowledgements: This work was carried out within the framework of the COST CA15209 Action "European Network on NMR Relaxometry

O4 New blue fluorescent Zinc(II) complexes with high quantum yield based on tuneable 1,3-substituted-imidazo[1,5-a]pyridine ligands

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New Zinc(II) complexes have been synthesized and studied employing fluorescent 1,3-substituted imidazo[1,5-a]pyridine derivatives introducing both electron-donating and electron-withdrawing moieties in position 3 on the ligand skeleton. The obtained compounds have been characterized with different spectroscopic techniques, their structure has been defined by single-crystal X-ray diffraction, mass spectrometry and elemental analysis, their optical properties have been discussed in relation to their chemical structures. The comparison between the emission spectra of the free ligand and corresponding Zinc(II) complexes shows an intense hypsochromic shift, due to the modification of the ligands conformation upon metal coordination, and an extraordinary increment of the quantum yield after complexation.

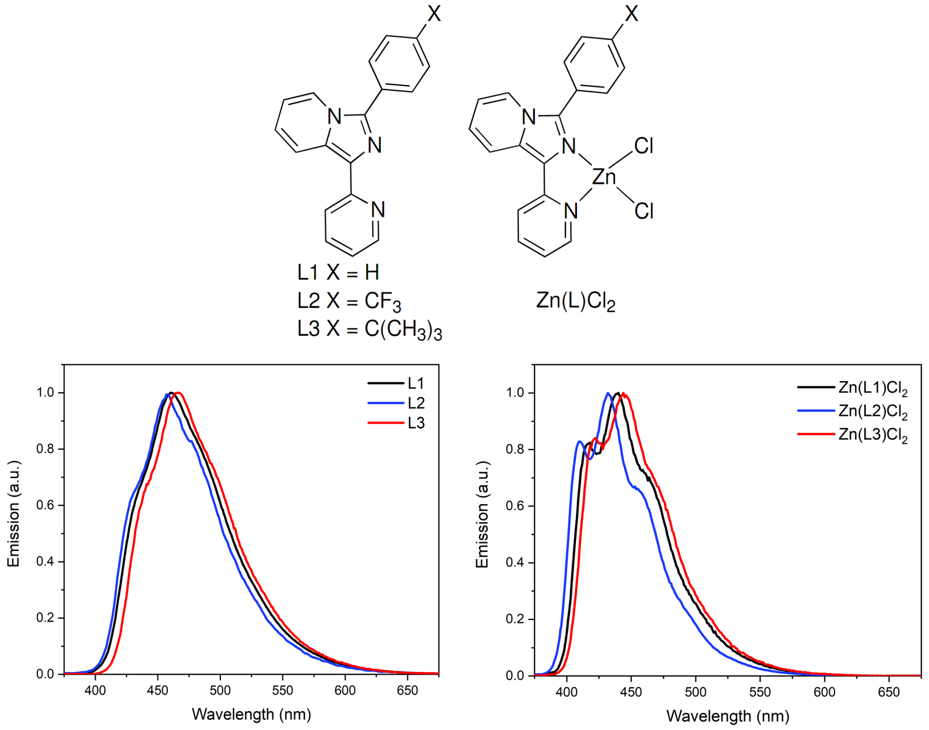

***Figure 1**: Structures and emission spectra of L (imidazo[1,5-a]pyridine ligands) and corresponding* $Zn(L)Cl_2$ *complexes in dichloromethane solution.*

O5 Interplay between zinc and copper binding to metallochaperone Atox1 and the N-terminal domain of Menkes ATPase.

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Cu is crucial for a number of key human enzymes and its trafficking pathways exhibit high protein-protein specificity. In humans, the metallochaperone Atox1 transports Cu(I) to the metal-binding domains (MBDs) of Menkes (Atp7a) and Wilson (Atp7b) disease proteins, located in the Golgi [1]. The Cu(I) transfer between Atox1 and the first MBD of Atp7a (Mnk1) occurs through the formation of an Atox1-Cu(I)-Mnk1 heterodimeric adduct [2], in which the Cu(I) ion connects the Cys residues of a conserved CxxC motif present in each protein [3]. However, the precise mechanism by which Cu-ATPases receive Cu from Atox1 is not yet clear. Furthermore, it is not understood why six MBDs are required in humans, while only one or two are present in the bacterial and yeast transporters. A separate role in sensing Zn(II), and perhaps other metals, is an intriguing possibility for some domains, and could provide a direct link between Zn-mediated signalling and Cu transport [4]. Hence, we investigated by NMR the interaction of $Zn(acetate)_2$ and its membrane-permeable complex with thiomaltol ligand, $Zn(tma)_2$ [5], with both the *apo* and Cu(I)-loaded forms of Atox1 and Mnk1 as well as with the Atox1-Cu(I)-Mnk1 heterodimeric complex. We found that Zn(II) can interfere with the rapid equilibrium of Cu(I) exchange between Atox1 and Mnk1 and trigger vectorial Cu(I) transfer from the metallochaperone to the target domain of Menkes ATPase. The interplay between Zn(II) and Cu(I) ions can influence the conformation of the N-terminal tail of Atp7a and its interaction with Atox1, thus modulating the trafficking of proteins from the Golgi to the plasma membrane, an essential process recently recognized as relevant for cancer cell migration and metastasis [6].

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O6 M(bpy-R)(CO)$_3$X (M=Mn, X=Br or M=Re, X=Cl) catalysts for homogeneous and heterogeneous CO$_2$ electroreduction

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Converting carbon dioxide via electrochemical reduction into useful chemicals and fuels for energy storage is an attractive and promising approach. It represents also an excellent strategy for mitigating the challenges of intermittent renewable energy production. Despite the numerous advantages of heterogeneous electrocatalysis, clever integration with the homogeneous counterpart allows a rational design of the catalysts, by tuning both the metal center and/or the ligand. Bipyridine transition metal complexes represent one of the most studied classes of molecular electrocatalysts. The role of the substituents on the electrochemical properties and the related overpotentials required for CO_2 transformation have been analyzed on a series of new 2,2'-bipyridine metal complexes fac-M(bpy-R)(CO)$_3$X (where M = Mn, X = Br or M = Re, X = Cl).[1] Electrochemical behaviors of the complexes in acetonitrile under Ar and their catalytic performances for CO_2 reduction with added water and MeOH have been investigated by cyclic voltammetry and controlled potential electrolysis. The complexes carrying only electron withdrawing groups lose their catalytic activities towards CO_2 reduction, whereas electron donor ligands and push-pull systems display electrocatalytic current enhancement under CO_2 atmosphere. The only detected reduction product by GC analysis is CO. In the case of a Mn bipyridine derivative in which two pendant phenolic groups act as local proton source capable of reducing CO_2 even in anhydrous acetonitrile. In this case a considerable amount of HCOOH was also detected.[2,3] Impressive results have been obtained by using the (fac-Mn(apbpy)(CO)$_3$Br) (apbpy = 4-(4-aminophenyl)-2,2′-bipyridine) complex grafted electrochemically onto carbon cloth serves as an electrocatalyst in the aqueous reduction of CO_2 to syngas.[4] A faradaic efficiency of around 60% for CO and 40% for H_2 at −1.35 V is achieved together with a productivity rate higher than 870 $\mathrm{Nl_{CO}\ h^{-1}\ g_{Mn}^{-1}}$ at turnover numbers of up to 33200 during 10 hours of operation.

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O7 Human Serum Albumin and Cisplatin, a Still Ongoing Debate.

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Since the first approval of cisplatin for cancer treatment in 1978, a lot of attempts have been carried out to characterize in detail its interactions with serum albumin, by far the most important and most abundant plasma protein. The state of the art of those studies was recapitulated by Keppler and coworkers in an extensive review article which appeared in Chem. Rev. in 2006. Yet, the general picture was still rather incomplete at that time due to the lack of crystallographic data. Here, we report on the main achievements obtained on this system in the period 2006-2018 and try to describe what is now clearly ascertained and what are the still open issues. Remarkably, a detailed structural characterization of this metallodrug/protein system was recently obtained thanks to the resolution of the crystal structure of a cisplatin/serum albumin adduct; crystallographic results were nicely complemented by independent MS studies. In turn, metallomics investigations permitted to monitor platination of this serum protein in real blood samples. Thus, a rather complete description of the system was gained. In addition, the biological profile of cisplatin/serum albumin adducts was drafted in a specific study and its pharmacological implications discussed. The relevance and the impact of these novel results are here evaluated.

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Acknowledgements: The authors thank Beneficentia Stiftung (Vaduz, Liechtenstein), AIRC and Fondazione Cassa Risparmio Firenze for founding the projects "Advanced mass spectrometry tools for cancer research: novel applications in proteomics, metabolomics and nanomedicine" (Multi-user Equipment Program 2016, Ref. code 19650). CIRCMSB is also acknowledged. TM thanks University of Pisa (Fondi Ateneo Rating 2018) and Fondazione Italiana per la Ricerca sul Cancro, Project Code: 18044. JG greatly acknowledges funding from CIHR-THRUST and Alberta Innovates Health Solutions (HIS grant 201000689).

O8 Porphyrin-based systems: homogeneous catalysts for the CO_2 cycloaddition to epoxides and aziridines

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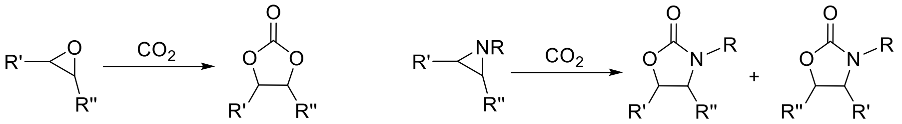
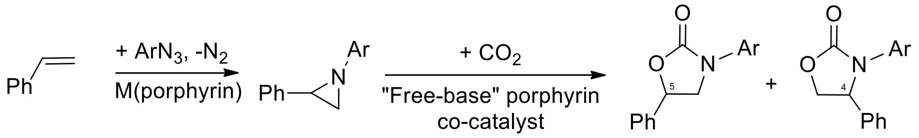
The direct insertion of carbon dioxide (CO_2) into three-membered rings, such as epoxides and aziridines, represents a relevant strategy for obtaining cyclic carbonates and oxazolidinones, which are two useful classes of fine chemicals (scheme 1).



***Scheme 1**: Synthesis of cyclic carbonates and oxazolidinones starting from epoxides and aziridines*

The synthesis of these compounds can be efficiently catalyzed by a combination of porphyrin-based systems and various co-catalysts under homogeneous conditions.[1] Considering the importance in developing eco-friendly catalytic procedures, we are currently studying the cycloaddition of CO_2 to epoxides and aziridine by using the dual tetrabutyl ammonium salt/porphyrin systems which mediate the formation of many different oxazolidinones in good yields and regioselectivities.[2] Moreover, considering our expertise in performing aziridination reactions by using metal porphyrin catalysts,[3] the synthesis of *N*-aryl oxazolidinones was investigated by applying a *two-step procedure* where the formed aziridine can be transformed into the corresponding oxazolidinone without being neither isolated nor purified (scheme 2).[4]



***Scheme 2**: Two-step procedure for transforming N-aryl azides into N-aryl oxazolidinones*

Finally, a mechanistic investigation of the CO_2 cycloaddition processes is in progress to suggest a catalytic cycle in order to pave the way for designing more active and efficient catalytic procedures.

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O9 Inhalable Calcium Phosphate Nanoparticles for Cardiac Drug Delivery

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Cardiovascular diseases (CVDs) are a worldwide growing problem that cause 17.3 million annual premature deaths. This situation prompts to identify new therapeutic compounds as well as to develop efficient drug-delivery systems for the treatment of CVDs. Among therapeutic compounds, microRNAs (miRs) and peptides are of great interest, since they are key regulators of cardiac dysfunction and protein activity [1]. However, the approaches that employ therapeutic miRs or peptides are still not optimal, since *in vivo* delivery has resulted so far to be inadequate [1]. Nanoparticles (NPs) delivery platforms hold great promise to overcome such limitations, providing a strategy for efficient drug-delivery approaches. The aim of the present work was the generation of effective NPs formulation for the delivery of novel therapeutic drugs into cardiac tissue. Calcium phosphate nanoparticles (CaP NPs) have been selected, since they possess superior biocompatibility and biodegradability compared to other NPs, and they are able to bind a significant number of therapeutic agents [2]. Synthesis of CaP NPs loaded miRNs or peptide was performed according to a new, straightforward protocol employing citrate as a stabilizing agent and regulator of crystal growth [3]. Inhalation of CaPs NPs allows for rapid translocation of CaPs from the pulmonary tree to the bloodstream and to the myocardium, where their cargo is quickly released. Treatment of a rodent model of diabetic cardiomyopathy by inhalation of CaPs loaded with a therapeutic mimetic peptide that we previously demonstrated to improve myocardial contraction resulted in restoration of cardiac function. These results demonstrate that inhalation of biocompatible NPs loaded bioactive molecules represents a pioneering approach for the treatment of heart failure.

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O10 Selective catalysts driven polyols oxidation in sustainable conditions

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In order to prevent pollution and environmental problems and to achieve the sustainable principles the scientific communities are now committed to develop novel and cost-effective methods to shift from the use of fossil carbon to renewable carbon. Recently, in order to substitute nonrenewable fossil resources such as crude oil, coal, and natural gas with renewable carbon sources such as biomass, including lignocellulose and vegetal oils, as a sustainable feedstock several efforts have been done. The renewable C can be used to obtain biofuels[1], commodity chemicals, high-added-value products and new biobased materials such as bioplastics.[2] Recently, even CO_2 has been taken into serious consideration as a building block for chemicals or as a source of carbon for fuels.[3] Among renewable feedstock, lignocellulosic biomass has attracted attention owing to its potential as a source of a wide range of platform chemicals such as C6-polyols, 5-hydroxymethylfurfural (5-HMF), levulinic acid (LA) or formic acid (FA) (Figure 1).

The oxidative cleavage of glucose (or fructose), has been considered as a route to biomass-based production of monocarboxylic and dicarboxylic acids, a technology that has not yet reached a "sustainable" level today. Recently, efforts have been made to convert C6 into lactic acid, succinic acid or oxalic acid.

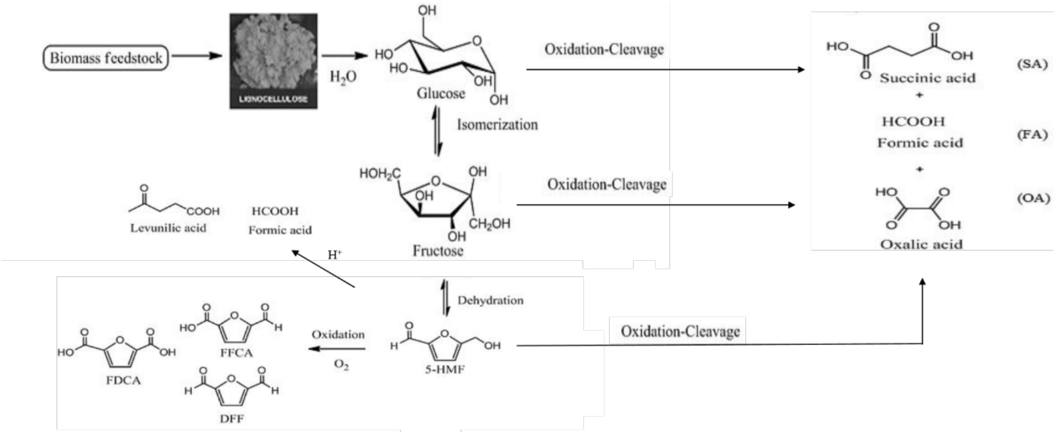

***Figure 1**: Processes for the conversion of lingocellulosic biomass into chemicals*

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O11 From natural enzymes to synthetized catalyst: the nitrile hydration. Insights from theory

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The organic nitriles are widely adopted by industries in different production fields, like synthesis of plastic, pesticides, water treatment reagents and other pharmaceutical and chemical products. In particular, nitriles are important starting reagents in the production of amides, adopted as drugs in tuberculosis and other diseases. According with those requests, the industrial production of amides from nitriles is centred around the use of microbiological synthesis, mediated by Fe(III)- and Co(III)-dependent enzymes (nitrile hydratase).[1] Recently similar catalytic activity, observed in natural enzymes, has been registered, for the first time, for a synthetized Mn(I)-containing complex (5-Mn, see ***Figure 1***).[2] On the basis of accurate structural characterization different catalytic mechanisms have been proposed but the debate is still open. Furthermore, kinetical study has been reported exclusively for aromatic substrates.[2] For these reasons, systematic DFT investigation, in comparison with the respective metal-dependent natural enzymes,[1] has been undergone on both aromatic and aliphatic substrates in order to provide atomistic details on the proposed mechanism.

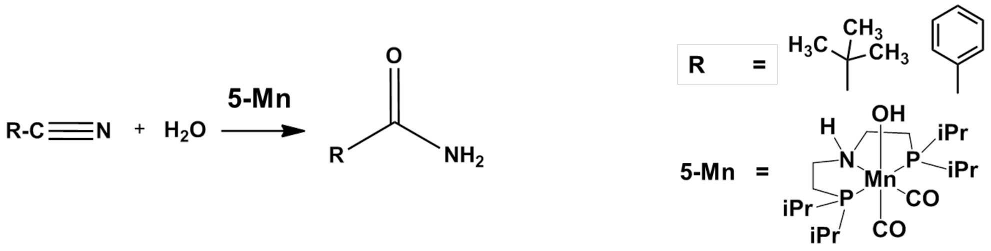

Figure 1*: generic scheme of nitrile hydration catalysed by 5-Mn complex .*

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Acknowledgements: *Financial support from the Università degli Studi della Calabria, Dipartimento di Chimica e Tecnologie Chimiche (CTC), is acknowledged.*

O12 Catalytic C-H Activation Reactions Catalyzed by Monocarbonyl Ruthenium Complexes

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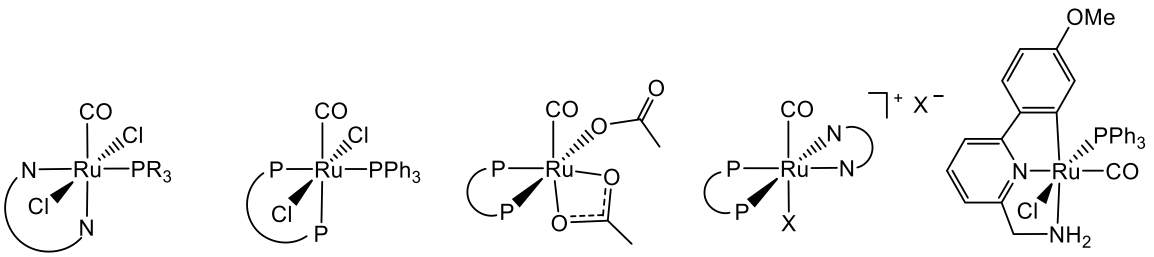
Mono and dicarbonyl ruthenium complexes have attracted a great deal of attention in homogeneous catalysis on account of their ability to promote a number of catalytic transformations, including hydrogenation, dehydrogenation and borrowing hydrogen reactions involving alcohols and carbonyl compounds.

We report herein the preparation of a series of monocarbonyl compounds with (chiral) phosphine and nitrogen ligands (Figure 1), which display high catalytic activity in transfer hydrogenation and *N*-alkylation reactions. Some applications to the conversion of biomass derivatives and synthesis of heterocyclic compounds are presented [1, 2].



X = OAc, Cl; R = Cy, *i*Pr

***Figure 1**: Monocarbonyl ruthenium complexes*

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O13 How platinum anticancer drugs affect Atox1 and copper ion interaction: a crystallographic investigation

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Copper is a trace element essential to the health of all living organisms. Although it is present in trace amounts in the human body, this ion allows the smooth running of important processes, such as cell proliferation and angiogenesis, as well as the proper folding of cuproenzymes. However, copper can also be very toxic, therefore its concentration has to be tightly controlled. Its equilibrium is entrusted to Atox1, a copper binding protein able to transport the metal ion from the cytosol to trans-Golgi network or secretory vesicles [1]. By using X-ray crystallography, we investigated how the presence of platinum-based anticancer drugs affects the interaction between this metal ion and Atox1. Our results point out that in the case of Atox1 dimer formed in the presence of copper, platinum ion is able to replace partially copper ion, thus leading to a disruption of the delicate process that regulates copper level in the cell [2]. (Figure 1). These results strengthen the hypothesis that platinum-based anticancer drugs could induce copper dyshomeostasis with important consequences in processes related to cancer, such as cell migration and metastasis.

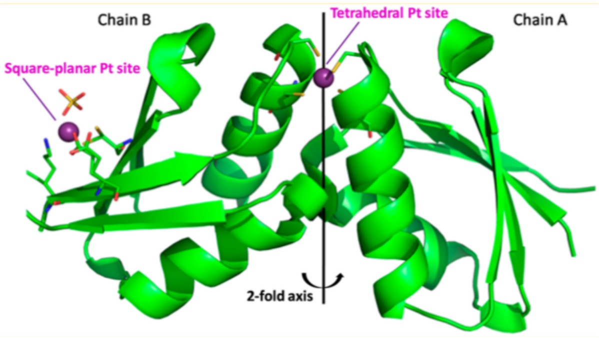

Figure 1*: Crystal structure of Atox1 crystallized in the presence of* $[Pt(R,R\text{-}DACH)(H_2O)(SO_4)]$

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O14 Ethanol conversion over copper based catalytic systems.

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(Bio)Ethanol produced by fermentation of lignocellulosics is expected to become a primary intermediate in the new industrial organic chemistry based on renewables.

Many studies are dealing with the manufacture of acetic acid, ethylacetate, acetone, 1-butanol, butadiene, isobutene, by single step processes starting from (bio)ethanol. Among the secondary intermediates, (bio)acetaldehyde may play a relevant role since it has been recognised as one of the main platform molecules for the production of several industrial chemicals [1]. For the dehydrogenation of alcohols into carbonyl compounds, systems such as Cu-ZnO, Cu-SiO_2, Cu-Al_2O_3, Cu-ZnO-Al_2O_3, Cu-$MgAl_2O_4$ have often been studied. Recently, our group worked on Cu-ZnO-Al_2O_3 and tested the performances to obtain selectively acetaldehyde [2]. Cu- based catalysts can be applied as catalysts converting ethanol into different categories of chemicals as certainly aldehyde. By tailoring support-metal interaction, acido-basic properties, metal clusters size and metal-support interaction and possibly with the addition of promoters, it would be possible produce also C4 oxygenates molecules, aromatics and/or hydrocarbons fractions usable into gasoline. The aim of this work is to develop new Cu-based supported catalysts for (bio)ethanol conversion into high added value chemicals. To this purpose copper-based catalysts with different Cu loadings (10% and 30% as $wt_{CuO}*100/wt_{support}$) were prepared by conventional wet impregnation method by using $Cu(NO_3)_2*3H_2O$ aqueous solution and different support, i.e., Al_2O_3 and $ZnAl_2O_4$. All the catalysts (fresh and spent) were characterized by XRD, FT-IR and DR-UV-Vis spectroscopies, Field Emission SEM microscopy. The catalysts have been tested in a fixed bed tubular quartz flow reactor at different ethanol partial pressures and by varying contact time and temperatures. The results so obtained will be described and commented.

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O15 Reactive carbonyl species and copper(II) as competitive effectors of α-Synuclein

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The main histological hallmark of Parkinson's disease (PD) and dementia with Lewy Bodies (DLB) is the accumulation of α-synuclein (αSyn) in several brain regions. These common synucleinopathies, such as other neurodegenerative disorders, seem to develop by the increase of amyloidogenesis, oxidative stress and metal dyshomeostasis [1,2].
In particular, copper(II) accumulates into the cerebrospinal fluid and Lewy bodies of PD patients and promotes αSyn aggregation and fibrillation [3,4]. Reactive carbonyl compounds (RCS), like 4-hydroxy-nonenal (HNE) and acrolein (ACR), also bind to αSyn both *in vitro* and *in vivo* [5,6].
Notwithstanding these findings, the mutual effects of RCS and Cu(II) on αSyn structure and function has never been investigated. Therefore, we explored more thoroughly the dose- and time-dependent effects of ACR on αSyn using a proteomic approach based on Ultra Performance Liquid Chromatography (UPLC) coupled with High-Resolution Mass spectrometry (HRMS). We also evaluated the influence of copper(II) ions on these chemical modifications and the effects of ACR and copper(II) ions on αSyn conformation and aggregation by circular dichroism, fluorescence and dynamic light scattering measurements.

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O16 Chemical Vapor Deposition of 2D Materials

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Currently, the “hype” on graphene and, specifically, on its unique combination of transparency, conductivity and flexibility is accompanied and supported by a renewed interest in families of different layered materials such as the transition metal dichalcogenides, TMDs, (MoS_2, WS_2, WSe_2, etc.). Concerning the production methodologies, mechanical exfoliation of bulk-layered materials allows the isolation of single and few-layer crystals with high quality and limited lateral size (tens of microns) that are suitable for fundamental studies. On the other side, the growth of large area single and few-layer films, as needed for technological applications, relies on the chemical vapor deposition, CVD, methodologies.

Graphene can take advantage from a metal catalyzed CVD methodology that allows a large area film growth self-limited to the first layer. However, CVD graphene production is characterized by very high cost and a poor control of the graphene polycrystalline nature (grain sizes and orientations). Moreover, the growth of a uniform single layer graphene is still challenging since bilayer graphene islands are typically formed during the CVD process. On the other side, the CVD synthesis of few layer continuous films of TMDs is still a critical issues. This strongly limit the development of applications based on TMDs due to their strong thickness/band structure correlation (indirect-to-direct bandgap transition going from bulk to monolayer form).

We presents chemical strategies for the CVD growth graphene and TMDs (WS_2 and MoS_2). These include hydrogen plasma-chemical treatment of copper substrate before graphene growth for minimizing the surface density of bilayer islands [1]; the use of volatile metal precursors in a batch chemical reactor for the deposition of few layer continuous films of WS_2 and MoS_2 with homogeneous thickness on the centimeter scale [2].

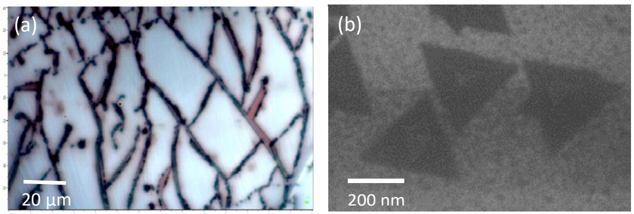

Figure. (a) Optical image of CVD graphene on copper. Copper oxidation between graphene grains defines the polycrystalline nature of graphene film. (b) SEM image WS_2 crystals grown by CVD on graphene.

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O17 Solution and solid-state NMR study of saponite clays intercalated with paramagnetic chelates

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Clays are versatile materials able to incorporate a wide range of guest species with different functionalities. The introduction of *f*-block elements, as ions or complexes, in synthetic clays lead to the development of novel lamellar systems with interesting optical and magnetic properties. Recently, the intercalation of two positively charged Gd^{3+}-chelates, based on amino-functionalized DOTA and AAZTA macrocycles with different hydration state of the metal ion, in the gallery of saponite has given relevant information on the chemical nature and the accessibility of exchange sites of these novel paramagnetic materials.[1] In this work, we synthesized a novel Gd^{3+}-complex based on an amino-derived TETA macrocycle, characterized by the absence of inner sphere water molecules. The complex was confined in saponite clay thus obtaining a paramagnetic material (GdL/SAP) (*Figure 1*). ^1H-NMR relaxometric investigations of the aqueous suspensions of GdL/SAP, as a function of applied magnetic field strength and temperature provide insights into the water diffusion mechanisms in the interlamellar space of the saponite. Increased longitudinal relaxivity at high magnetic fields, compared to the free Gd^{3+} complex, established the reduction of the local mobility of the confined GdL and the decrease of water diffusion through the interlamellar space. Such behavior is due to the strong chemical interactions between the complex/water molecules and the layered inorganic framework as investigated by solid-state NMR measurements performed on a diamagnetic analogue of the clay YL/SAP.

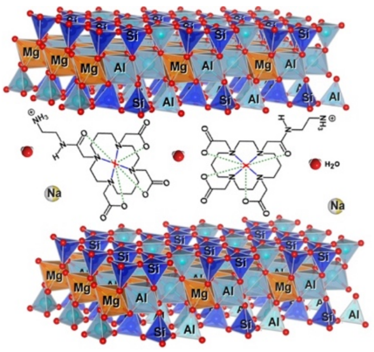

Figure 1*: The general structure of the intercalated saponite clay with TETA chelate (X = Gd^{3+} or Y^{3+}).*

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Acknowledgements: This work was carried out within the framework of the COST CA15209 Action "European Network on NMR Relaxometry.

O18 Point Defect Formation via Reactions at Chalcogenide Surfaces

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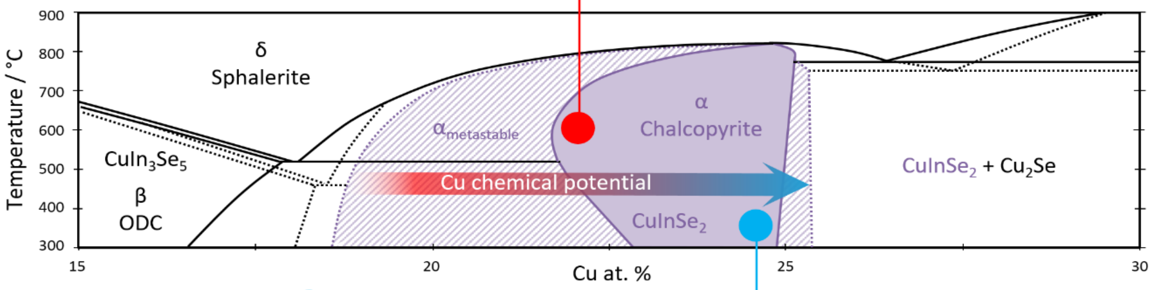
Anion vacancies are a source of degradation for *lead halide perovskites* (LHP), a class of compounds known for the striking lab-scale photovoltaic (PV) device performance [1].

The commercially established *chalcopyrite* PV, which is based on the distinct class of chalcogenide compounds, is also impaired by anion vacancies [2]. Indeed, this also applies to chalcogenide-based topological insulators, representing a severe bottleneck for the progress of a new generation of information and communication technologies [3].

This study shows that reactions occurring at the surface of $CuInSe_2$ at room temperature involve the generation of point defects in the near-surface region of the semiconductor. The findings reveal that the limited diffusivity of atoms at room temperature and a sizable phase homogeneity field [4] are the root causes for the formation of metastable point defects with detrimental optoelectronic effects.

While in LHP anion vacancies form due to the competitive halide oxidation, surface reactivity and the resulting extent of selenium loss in $CuInSe_2$ are shown to depend heavily on the relative chemical potential of the metal cations (Figure 1).

$$2[Cu_{(1-y-z)}(In_{Cu})_y(V_{Cu})_z]InSe_{2(s)} + \frac{3x}{2}O_{2(g)} \rightarrow xIn_2O_{3(s)} + 2[Cu_{(1-y-z)}(In_{Cu})_y(V_{Cu})_z][(In)_{1-x}(V_{In})_x]Se_{2(s)}$$



$$2[Cu(Cu_i)_z]InSe_{2(s)} + \frac{3x}{2}O_{2(g)} \rightarrow xIn_2O_{3(s)} + yCu_2Se_{(s)} + 2[Cu(Cu_i)_{z-y}][(In)_{1-x}(V_{In})_x][Se_{(1-y/4)}(V_{Se})_{y/4}]_{2(s)}$$

***Figure 1**: Portion of In_2Se_3-Cu_2Se pseudobinary phase diagram and point defect metastable equilibria.*

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Acknowledgements: *this research was funded by the FNR Luxembourg via the author's project GALDOCHS C14/MS/8302176 and by INL and the European Commission via the Marie Curie Cofund project n. 713640.*

O19 Labelling metallodrug candidates with fluorescent dyes: some relevant examples

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The study of metal based drugs represents an important branch of modern bioinorganic chemistry. The growing importance of this field is linked to the large success in Medicine of a few metal based drugs, either in clinical use or still experimental, in the treatment of cancer [1].

For these reasons, the study of intracellular biodistribution of metal based drugs through the utilization of confocal microscopy, has became a central topic in the field of Bioinorganic Chemistry. In this presentation two relevant examples of metallodrug labelling strategies, focused on the utilization of Anthracene derived and BODIPY probes will be discussed (Figure 1) [2].

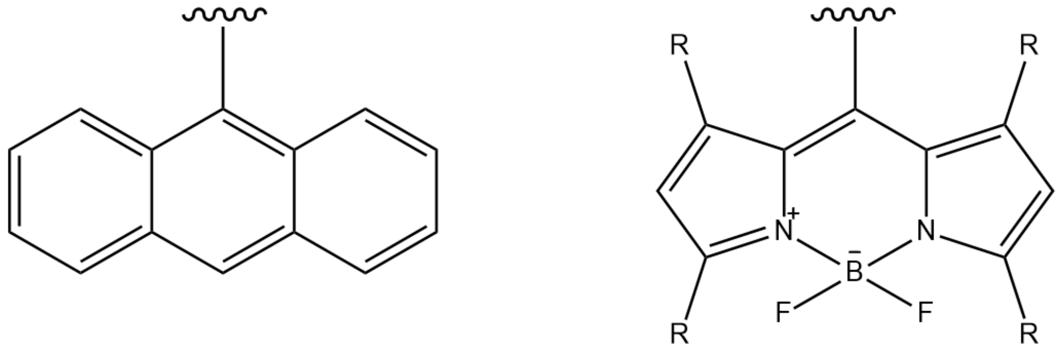

***Figure 1**: Anthracene and BODIPY scaffold.*

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O20 The reversible electronic energy transfer in quantum dots-based inorganic-organic nanohybrids

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Semiconductor nanocrystal Quantum dots (QDs) are emerging nanomaterials with exceptional photophysical properties [1,2] such as a broad band absorption spectrum with a relatively high absorption cross section, a sharp emission band endowed with a relatively small Stokes shift and high luminescence quantum yields compared to the most common organic fluorophores such as rhodamine or fluorescein [3].

Moreover, inorganic-organic quantum dot-based nanohybrids have been exploiting as novel triplet photosensitizers [4] since last few years. Although several examples of unidirectional triplet-triplet like energy transfer have been already reported [5], we recently developed the first example of the reversible, that is bidirectional, electronic energy transfer (REET) occurring between CdSe QDs and a suitable surface-bound chromophore [6].

In our nanohybrids, the emitting state of a suitably synthesized CdSe QDs sample undergoes an equilibration with the lowest triplet excited state of a pyrenyl surfactant giving rise to the thermally activated delayed luminescence and, ultimately, to the elongation of the lifetime of the nanocrystals. Here we report the possibility to tune the shape of the emission band of a bad polydisperse CdSe QDs batch and to detect selectively the signal of a certain CdSe QDs sample from a mixture of different-size QDs by taking advantage of the above described reversible electronic energy transfer.

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O21 Novel Curcumin-based radiotracers for Gallium-68 and Scandium-44.

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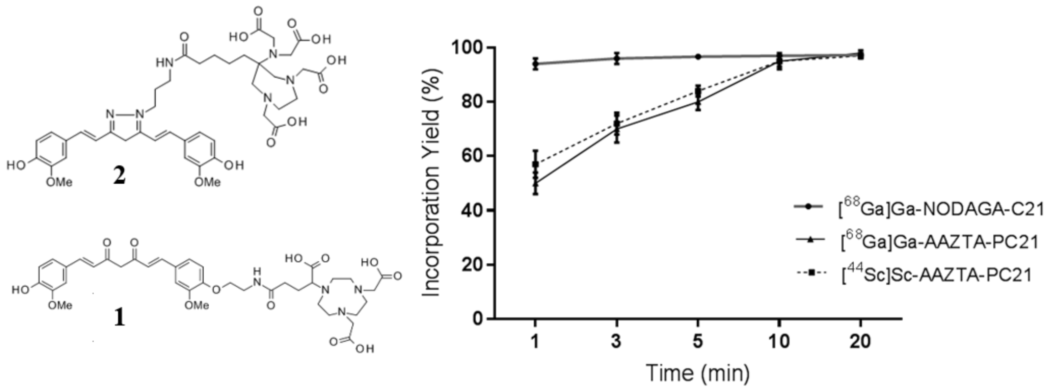
Curcumin metal complexes showed widespread applications in medicine and can be exploited as lead structures for developing new tracers for nuclear medicine application [1]. DOTA-curcumin was successfully labelled with gallium-68 and showed good water solubility and uptake in HT29 cells. Although the stability was significantly enhanced with respect to [68Ga]Ga-curcumin complexes, this still remains a concern and may be partially responsible for the biodistribution of [68Ga]Ga-DOTA-C21 [2]. Herein, the synthesis, chemical characterization and radiolabeling with gallium-68 and scandium-44 of two new targeting vectors based on curcumin scaffolds and linked to chelators (NODAGA-C21 and AAZTA-PC21, **Figure 1**) are reported.

Figure 1*: **Left** -Chemical structures of NODAGA-C21 (**1**) and AAZTA-PC21(**2**); **Right** - Incorporation yield of [68Ga]Ga-NODAGA-C21 (10 nmol, 95 °C), [68Ga]Ga-AAZTA-PC21 and [44Sc]Sc-AAZTA-PC21 (10 nmol, 30 °C) at different time points (n = 3, mean ± SD).*



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O22 Multitechnique Investigation for Rational Design of Molecular Spin Quantum Bits

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Molecular spins are quantum objects and, as such, they open the way to several applications: hybrid quantum architectures, quantum sensors, spintronics and quantum computation.[1] The great advantages in the use of molecules lie in their extraordinary tunability, of relevance for the realization of quantum-gates,[2] but they are also relevant for their scalability, and for their easy processing.[3,4] On the other hand, the spin relaxation times (T_1 and T_2) are still too short to warrant sufficient fidelity in gate implementation.[5] In this context, it is fundamental to identify the ingredients (metallic core, ligands, environment, etc.) that provide a lengthening of the spin relaxation times. I will present in this contribution the results obtained in the last years focusing on vanadium(IV)-based molecules through a multitechnique approach based on AC susceptibility, EPR and THz spectroscopy.

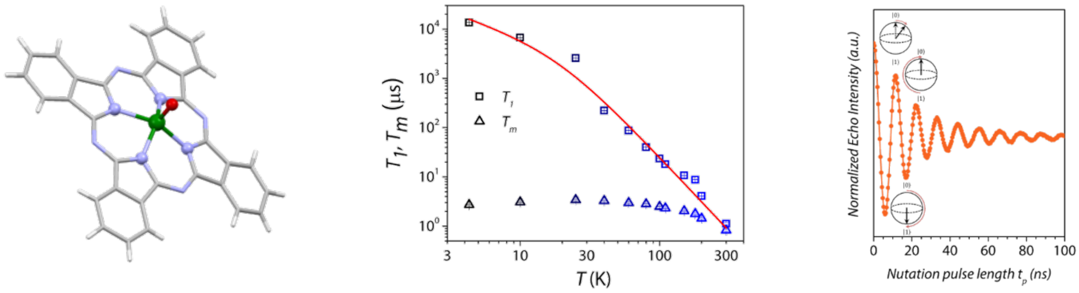

Figure 1*: (left) One potential molecular qubit is Vanadyl Phthalocyanine;(centre) Spin-lattice and spin-spin relaxation times of VOPc; (right) Rabi oscillations of VOPc performed by pulsed EPR*[4]

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Acknowledgements: *Italian MIUR, Fondazione Ente Cassa di Risparmio di Firenze, European Project SUMO and European COST Action MOLSPIN.*

O23 Unrevealing the real pigment composition of green tattoo inks

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Since losing their maverick image, tattoos are no longer fringe groups markings, but a widespread practice with estimated 120 million people tattooed worldwide in 2016[1]. This poses problems of safety of the materials injected under the skin. In spite of a foreseeable concern, no uniform regulation has been put in place to monitor the inks composition, determine the potential risks for human health and consequently restrict, whether necessary, the use of specific inks. There are indications on this issue by the ResAP(2008)1[2], dealing with cosmetics, and safety of the tattooing procedure, which were accepted in few countries in Europe, and largely neglected by the others. Meantime, new indications are being proposed by the Committee for Risk Assessment (RAC- Nov.2018)[3] and the Committee for Socio-Economic Analysis (SEAC- also Nov.2018)[3]. In this overall scenario, aiming at tackling tattoo inks safety, the first issue to address is their actual composition. Inks can be considered as roughly being composed of a pigment, imparting the colour, and a vehicle, ensuring the ink fluidity and asepticity. We selected green inks and performed multiple-techniques investigations to determine the actual pigment composition. In all of them, PG36, a hexabromine-decachlorine Cu-phthalocyanine was indicated as pigment both on the bottle labels and on the safety sheets, and PG7, a hexadecachlorine Cu-phthalocyanine was found, instead, which is restricted in countries where legislation on tattoo inks is enforced[4]. More false declarations on ink compositions were found, also for additional pigments in the inks, even if none of them is restricted[4]. Whitening agents such as TiO_2 nanoparticles may be present, but in this case, additional dispersing agent, with non-negligible Al and Si content were not declared. Issues on TiO_2 nanoparticles size are also to be considered for their potential cytotoxic aspect[4].

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O24 Optical sensing of heavy metal ions by sol-gel based plasmonic nanostructures

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The potential of plasmonics can be exploited in the field of nanostructured devices for sensing and environmental applications. Sensing requires chemically stable and optically tunable dielectric platforms, which should be properly functionalized by using molecular compounds, as fluorophores, able to recognize different analytes, particularly heavy metal ions. In the present work we have developed an innovative sol-gel composite system (Figure 1) where Fluorescein Isothiocyanate (FITC) has been grafted on the plasmonic and silicon surfaces.
The sol-gel method was used and optimized to control the thickness of silica layers on plasmonic surfaces[1]. The silica layers were functionalized with 3-aminopropyltriethoxysilane (APTES), as linker to graft FITC on plasmonic nanostructures forming a stable and covalent bond[2]. The resulting films were characterized via atomic force microscopy (AFM) and contact angle to check the thickness and the surface wettability[3]. The plasmonic platforms were investigated to verify luminescence and sensing properties using different metal cations.

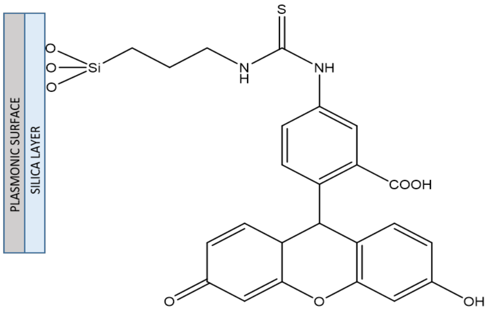

Figure 1. Sol-gel composite system

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O25 Plasma Activated Liquid Media as new pharmacological formulations to exacerbate cell oxidative stress

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Researches on plasma in or remotely in contact with liquids have a long history. During the last 10 years atmospheric pressure plasmas have shown great promise for the treatment of liquids of biological interest for therapeutic purposes [1-2]. In this paper a sealed DBD system and a controlled gas environment were used in order to produce plasma activated liquid media and stimulate eradication of cancer cells of very aggressive tumors like pancreatic cancer and melanoma mediated by the content of reactive oxygen species (ROS) or encourage wound healing by means of a combination of produced reactive oxygen and reactive nitrogen species (ROS and RNS) in the liquid medium as in case of brain wound healing. In this way Plasma Activated Liquid Media (PALM) were obtained. The modified Petriplas+ source utilized in this research is composed by a DBD setup designed in collaboration with the Leibniz Institute for Plasma Science and Technology (INP). Hydrogen peroxide and nitrite ions were dosed in DMEM 10% FBS showing that the [H_2O_2] increases while the [NO_2^-] decreases with the content of O_2 in the gas feed reaching values up to 6.00±0.11 mg/l for H_2O_2 and up to 1±0.04 mg/l for nitrite ions. In case of primary astrocytes, results showed that a higher amount of ROS species including H_2O_2 negatively affect cell adhesion while a different cell migration is observed depending on [ROS] and [RNS] species in the PALM. Thanks to the ESR investigation of PALM of PALMs, it seems that in complex system like cell culture medium the primary NO –the one coming from the discharge–would be involved in promoting certain biological responses, not directly, but only through one of its derivatives such as nitrite.

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Acknowledgements: *Prof. K-D Weltmann and Mr M. Schmidt are gratefully acknowledged for the cooperation offered with the Petriplus+ plasma source. Mr S Cosmai (NANOTEC, Bari, ITA) and Mr D. Benedetti are acknowledged for the technical support.*

O26 Self-Assembling in Water Soluble Ir(III) Complexes: From Hydrogels to Nanostructured IrO_2 Thin Films

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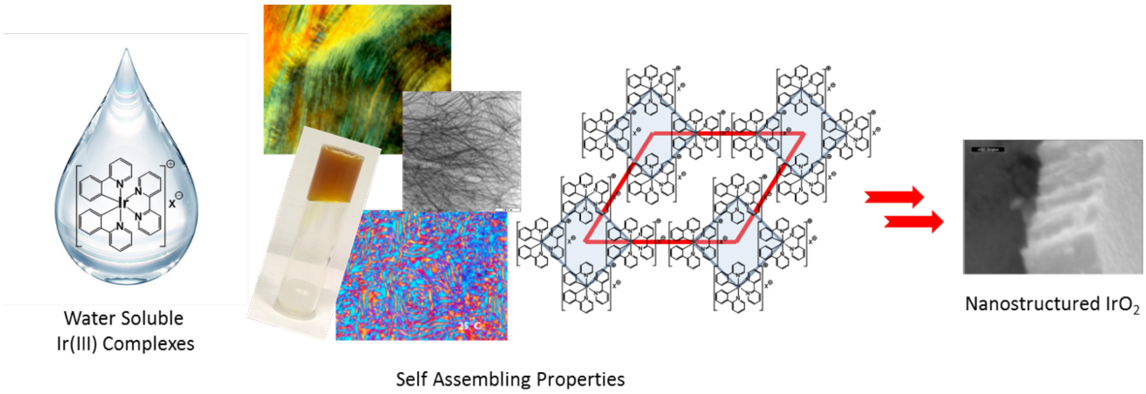
The present communication will illustrate a series of cationic water soluble Iridium (III) complexes. According to the choice of ligands completing the metal coordination sphere, and the nature of the counter anion used, high water solubility can be induced. In some cases, true lyotropic liquid crystal behaviour can be observed and/or highly organized hydrogel phases can eventually be promoted.[1] The supramolecular organization of the self-assembling properties of these Ir(III) complexes will be comprehensively discussed. Such high order in water phase has been finally exploited to access to nanostructured thin films of IrO_2.[2]



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O27 (Oral withdrawn) The coordination chemistry of a unique zwitterionic ligand

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The reaction of $Ph_2P(NH)PPh_2$ with EtNCS yields $EtNHC(S)PPh_2{=}NP^+Ph_2C(S)N^-Et$ (Figure 1, HEtSNS), together with three other products [1]. Nevertheless, HEtSNS can be prepared in quantitative yield. This molecule is a zwitterionic and amphoteric ligand, structurally flexible, with variable charge and denticity. HEtSNS can be deprotonated giving the dianion-cation $EtSNS^-$ or protonated to cationic H_2EtSNS^+. All the three species act as ligands (S,N,S; S,S; N,N,N; □-S,S; S), adapting to the chemical and sterical coordination requirements of the metal centres. Studying the coordination properties of HEtSNS is a chemical entertainment; nonetheless, its metal complexes (Cu, Ag, Au, Rh, Pd, Ru) possess peculiar qualities.

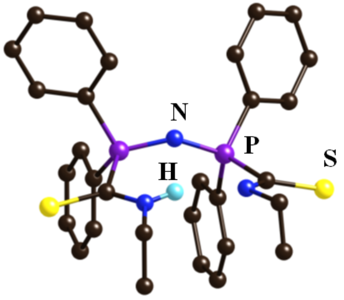

***Figure 1**: Solid state molecular structure of HEtSNS*

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O28 NIR-light-driven generation of reactive oxygen species using Ru(II)-decorated phospholipid-coated upconverting nanoparticles

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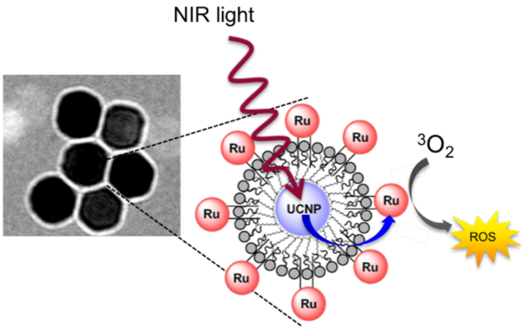
The biological application of ruthenium anticancer prodrugs for photodynamic therapy (PDT) is restricted by the need to use poorly penetrating high-energy photons for their activation, i.e. typically blue or green light. Upconverting nanoparticles (UCNPs), which produce high energy light under near-infrared (NIR) excitation,[1] may solve this issue, provided that the coupling between the UCNP surface and the Ru prodrug is optimized to produce stable nanoconjugates with efficient energy transfer from the UCNP to the ruthenium complex. Herein, we report on the synthesis and photochemistry of a UCNPs and a Ru(II) polypyridyl complex which is an efficient and photostable PDT photosensitizer. A water-dispersible, negatively charged nanoconjugate UCNP@lipid/Ru was prepared by the encapsulation of UCNPs in a mixture of amphiphilic phospholipids and complex (Scheme 1). A non-radiative energy transfer efficiency of 12% between the Tm^{3+} ions in the UCNP and the Ru^{2+} acceptor was found using time-resolved emission spectroscopy. Under irradiation with NIR light (969 nm), UCNP@lipid/Ru was found to produce reactive oxygen species (ROS).[2]



***Scheme 1**: Schematic impression of the nanoconjugate system UCNP@lipid/Ru.*

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Acknowledgements: This research was partially funded by The Holland Research School for Molecular Chemistry (HRSMC), Short Term Mobility of National Research Council (CNR), European Research Council, and COST Action CM1403.

O29 - Winner of the PhD Prize: Reaching a new level of understanding of the bioinorganic chemistry of Pt drugs using MS-based techniques

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Platinum complexes have been widely employed in therapy since 1978 when the FDA approved the use of cisplatin for testicular cancer treatment, but its antiproliferative activity was already recognized in 1963. Since then, the scientific community have investigated the several interesting aspects regarding cisplatin distribution, its activation in the body and the interaction of platinum with biomolecules in general. However, the presence in solution of several species generated by consecutive substitution reaction of the labile chlorido ligands with water has hindered a fine characterization of the contribution of these species to the overall activity of the drug and of the binding motifs of the most active cisplatin aquacomplex with biological ligands.

In this contribution, I will briefly describe how we managed to decipher the differences in reactivity of species in which either one or two of the chlorido ligands have been substituted[1] and to obtain structural information about adducts of cisplatin with histidine and methionine[2] employing a combination of MS-based techniques ranging from high resolution mass spectrometry and ion-molecule reactions to IR multiple photon dissociation and ion mobility spectrometry. Moreover, we were able to extract from solution and characterize for the first time the encounter complex between the cisplatin aqua complex and model incoming ligands thus closely viewing its role in the substitution mechanism of platinum complexes.[3]

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Acknowledgements: *This work has been supported by Università di Roma "La Sapienza" (DR n. 3210/16), by the European Union's Horizon 2020 research and innovation program under grant agreement No. 731077, and by the French FT-ICR network (FR3624CNRS)*

O30 - Winner of the PhD Prize:
Study of new polar intermetallic compounds: synthesis, structural relations and real space chemical bonding analysis

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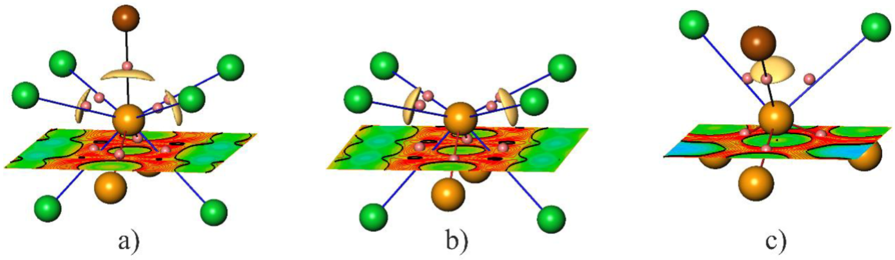
Metal-based materials have been heavily utilized by human civilization in any period of its development. In the last decades the discovery of new rare-earth intermetallic compounds, like $Nd_2Fe_{14}B$ permanent magnets, allowed incredible technological breakthroughs. Nevertheless, the challenging understanding of the main interactions governing the chemistry of intermetallics leads to our inability to predict their formation, structure and resulting properties. Consequently, these compounds are particularly interesting not only for their eventual applications but also for fundamental research. In this work, ternary *R*–*M*–Ge (*R* = rare earth metal; *M* = another metal) germanides were selected. The new R_2MGe_6 (*M* = Li, Mg, Al, Cu, Zn, Pd, Ag), R_4MGe_{10-x} (*M* = Li, Mg), $R_2Pd_3Ge_5$, $Lu_5Pd_4Ge_8$, $Lu_3Pd_4Ge_4$ and Yb_2PdGe_3 compounds were synthesized and structurally characterized. Many efforts were put into the stabilization of metastable phases, employing the innovative metal flux method, and into the accurate structure solution of twinned and modulated crystals. Cutting-edge position-space chemical bonding techniques, based on the Bader's Quantum Theory of Atoms In Molecules (QTAIM) [1] and the Electron Localizability Indicator (ELI-D) [2] were mainly applied to the La_2MGe_6 compounds. In order to correctly describe the Ge–*M*, Ge–La and also La–*M* interactions, going beyond the Zintl approximation, new tools were introduced: the Penultimate Shell Correction (PSC0) and the ELI-D fine structure based on its relative Laplacian (see Figure). The present results constitute a step forward in the comprehension of ternary germanides chemistry and a good playground for further investigations.



a) b) c)

***Figure**: ELI-D isosurfaces and its relative Laplacian's attractors (red spheres) for a,b) two-bonded and c) three-bonded Ge lone pair regions in La_2MgGe_6 compound.*

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O31 - Winner of the PhD Prize: Organometallic Iridium Complexes as Efficient Catalysts for Renewable Energy Applications

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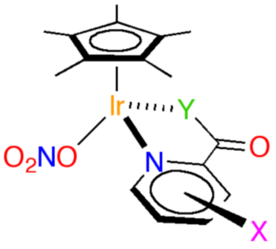
Water oxidation (WO) and formic acid (FA) dehydrogenation are two reactions of crucial importance in the field of renewable energy. WO to molecular oxygen is considered the ideal reaction for providing electrons and protons for the generation of any renewable fuel. Whereas FA dehydrogenation to H_2 and CO_2, as well as the reverse reaction, allows H_2 to be easily stored, transported and released. The possibility of exploiting WO and FA dehydrogenation strongly relies on the development of efficient catalysts.



Herein we show that organometallic iridium complexes bearing pyridine carboxylate (Y = O; X = OH, NH_2, H, Me, CF_3, NO_2) and amidate (Y = NR; R = H, Me) ligands are extremely active catalysts in WO[1] driven by CAN[2] and $NaIO_4$[3,4] and dehydrogenation of FA.[5] The activity of carboxylate complexes (Y = O) in WO strongly depends on the nature of the X-substituent in the pyridine ring. TOF values increase with decreasing the electron donor property of the pyridine ligand suggesting that a) water nucleophilic attack at the metal oxo moiety is the turnover limiting step or b) generation of the active species occurs through a detachment of the N,O-ligand. NMR studies allowed the nature of some intermediates of the oxidative degradation to be disclosed.

On the other hand, by combining DFT and NMR studies, we also show that protonation of the amidate functionality plays a critical role in modulating the activity of complexes (Y = NR) in catalytic FA dehydrogenation, providing a viable hydrogenation deactivation pathway.

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O32 UV and X-ray Excited Optical Luminescence in Cr^{3+} doped $ZnGa_2O_4$ thin films: a case study

Lidia Armelao[a,b], Federica Mian[a,b] Gregorio Bottaro[a,b], Marzio Rancan[a,b], Zhiqiang Wang[c], Yun-Mui Yiu[c], Tsun-Kong Sham[c]

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We report the thermally controlled synthesis of Cr doped $ZnGa_2O_4$ thin films and the evolution of its morphology, crystallinity and optical luminescence tracked with SEM, XRD, XPS, UV-visible absorption and emission spectroscopy as well as synchrotron-based X-ray Absorption Near Edge Structure (XANES) and X-ray Excited Optical Luminescence (XEOL). It is found that the as-prepared specimen is amorphous and exhibits no luminescence while annealing induces crystallization which markedly improves crystallinity at higher temperature. SEM, XRD and O, K-edge, Zn and Ga L-edge and Cr K-edge XANES show disordered to order phase transition upon annealing which is accompanied by the appearance of the N2 line characteristic of the persistent luminescence from Cr doped $ZnGa_2O_4$ where Cr^{3+} occupies the octahedral Ga^{3+} site. The N2 line correlates with the crystallinity of the sample in that the higher the annealing temperature, the better the crystallinity and the brighter the N2 line. It is also interesting to note that the optical luminescence from $ZnGa_2O_4$ which appears in the blue (420 nm) is completely quenched and the energy is transferred to the N2 luminescence in the red (696 nm), These results and their implications are discussed.

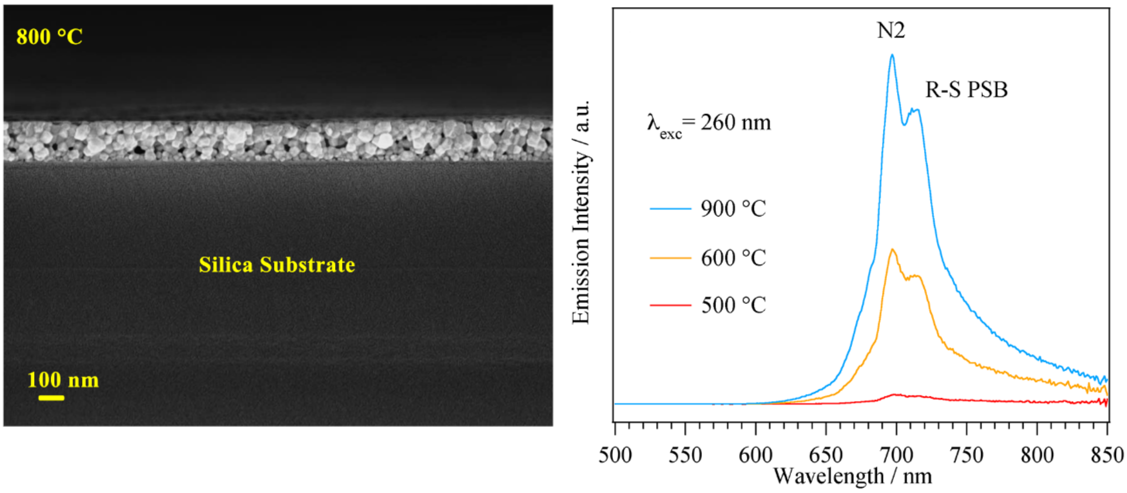

***Figure 1**: left: SEM cross section of $ZnGa_2O_4$:Cr^{3+} film annealed in air at 800 °C for 1h. Right: Emission spectra of samples annealed at different temperature evidencing the effect of the treatment on the emission intensity.*

O33 Bridging Solution and Solid-State Chemistry of Dicyanoaurate: The Case Study of Zn-Au Nucleation Units

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The formation complexes by employing metalloligands is a common strategy in the preparation of crystalline architectures. These complexes are often the result of a 'rational' use of molecular tectons but, in some cases, they seem rather to represent a serendipitous consequence of crystal packing. Most reported preparations consist of a simple combination of reagent solutions, left to stand until crystalline products are formed. However, in the absence of any clue as to the reactivity in solution, a crystal engineering approach that may control the passage from the solution to the crystalline state is impossible. The role played by solution-phase pre-organization and the formation or the growth of nucleation units is essential in the rational design of solid functional architectures and is currently one of the hottest research topics in supramolecular chemistry. [1] Dicyanoaurate ion is a tecton which is employed because of the versatility in the construction of functional coordination polymers characterized by a multitude of differing interactions and properties. [2] We decided to study the solution pre-organization in the case of bimetallic compounds based on dicyanoaurate, and with this aim we synthetized 9 crystalline compounds containing dicyanoaurate interacting with a family of zinc bis-chelated complexes. All the compounds have been structurally characterized and related to the solution chemistry of each specific system. With a multi-technique approach based on electronic spectroscopy, NMR, ESI-MS and X-ray Absorption Spectroscopy (XAS) at both Au L3- edge and Zn K-edge, we demonstrate the presence of pre-organization and oligomerization in solution and characterized the structure in solution of the common $\{Zn(L)_2[(\mu\text{-}CN)Au(CN)](H_2O)\}^+$ growth unit, deciphering the solid state structures on the results.

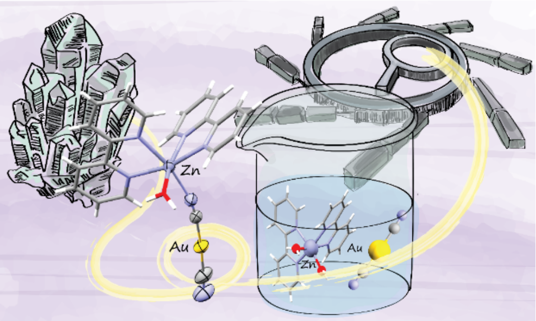

Figure 1*: Example of aggregation of the gold and zinc tectons.*

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O34 Synthesis and characterization of a new class of Ru-based photosensitizer

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Ruthenium(II) bipyridyl complexes have attracted great attention, due to their distinctive photophysical properties and chemical stability. In particular, the Ru(II) polypyridyl-based photosensitizers have proven effective in electron transfer, thanks to their strong Metal to Ligand Charge Transfer (MLCT) absorption band in the visible and relative long life-time of the triplet ^{3}MLCT state (in nanosecond scale). [1, 2] Several substituted bipyridyl-based complexes have been reported in the literature. [3] Nevertheless, the inherent stereogenicity of the metal center makes it hard to obtain pure compounds, thus hampering their applicability. [3] In this regard, many different types of heteroleptic Ru-based polypyridyl complexes have been developed. Here, we report the development of the *tris*-heteroleptic Ru(II)-polypyridine complex, shown in figure 1. It grants enhanced photosensitization, as well as reliability in bio-conjugation (high yield and purity, moderate activation conditions, and easily tuneable coupling strategies). In fact, the carboxyl functional group is suitable for derivatization and conjugation with different macromolecules and biological systems as photo-sensitizing component. Different spectroscopic and chromatographic analyses have been employed to validate the synthetic approach and to characterize the photosensitizer and its derivatives. Moreover, a DFT computational analysis has been carried out to better clarify the photophysical properties, finding out an excellent correlation between theoretical and experimental data.

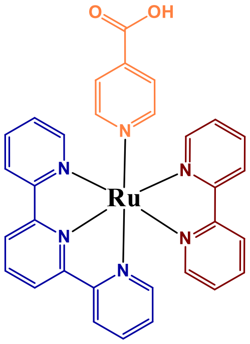

***Figure 1**: structural image of the synthesized Ru(II)-complex.*

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O35 Structural characterization of halide perovskites by X-ray measurements and advanced analysis

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The advent of new-generation X-ray sources, more sensitive and fast detectors discloses the possibility of deeper static and dynamic structural investigations. X-ray powder diffraction (XPD) and pair distribution function (PDF) measurements are sensitive to long and short-range order, which can be modelled by fitting procedures. Tiny structural changes induced in situ by varying external parameters (temperature, light) can be also detected by efficiently processing multiple measurements. In this case, the traditional approach to fit each measurement independently can be coupled with the new approach to apply multivariate methods such as Principal Component Analysis and Phase Sensitive Detection to the whole dataset [1]. Single and multiple XPD and PDF measurements has been here analysed for the high-sensitivity structural characterization of halide perovskites. We have investigated the role played by traditional molecular hosts, cyclodextrins (CD), to generate a hybrid perovskite-soft material, demonstrating that the interaction between CDs and perovskite precursors, MAI and PbI_2, leads to the formation of a supramolecular organic–inorganic hybrid framework importantly modifying the solution chemistry and the final film properties [2]. The multivariate analysis approach has been applied to in situ experiments to reveal the reversible generation, under illumination, of paramagnetic Pb^{3+} defects in $CH_3NH_3PbI_3$ perovskite [3], and to get new insights into its tetragonal-to-cubic phase transition under temperature changes.

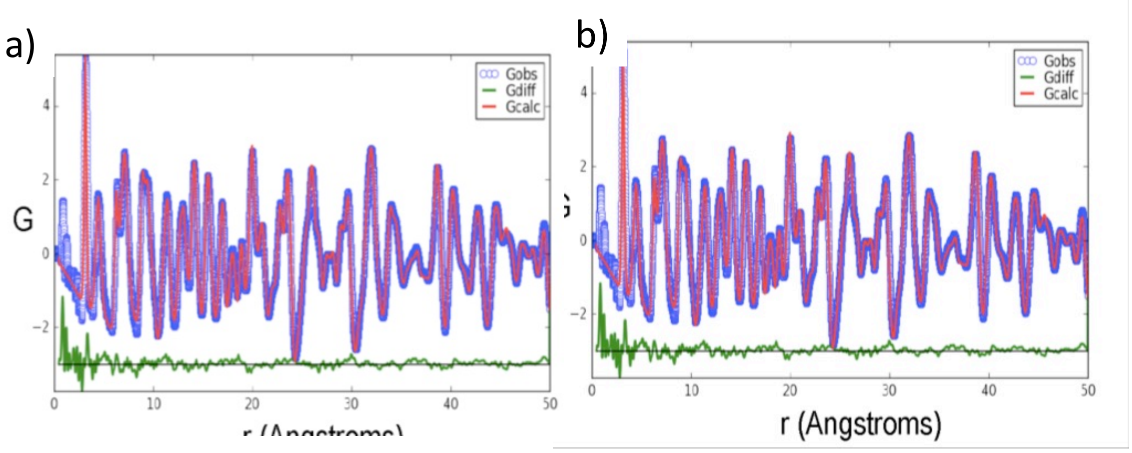

***Figure 1**: Fit of PDF by the $MAPbI_3$ tetragonal phase model (a) and scores obtained by PCA applied to the PDF data matrix in slices of 3 Å, for increasing interatomic distances (b).*

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O36 Mesoporous bioactive glasses doped with cerium investigation over enzymatic-like mimetic activities and bioactivity

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Mesoporous bioactive glasses (MBGs) were modified with cerium ions (Ce^{3+}/Ce^{4+}) to act as catalase and superoxide dismutase (SOD) mimetic materials. Our previous studies [1-3] revealed that the catalytic properties of bioactive Ce-containing glasses based on 45S5Bioglass® are influenced by: i) composition (presence/absence of P_2O_5); ii) Ce^{3+}/Ce^{4+} molar ratios. Moreover, the presence of cerium species drastically decreased the bioactivity in terms of Hydroxyapatite formation during bioactivity tests in vitro. So, we decided to add cerium to MBGs, a class of glasses with improved bioactivity with respect to classical molten glasses. MBGs exhibit a high surface area and their reactivity is increased with respect to the molten glasses; they are able to induce the formation of Hydroxyapatite over the surface within shorter times with respect to the 45S5Bioglass®. The catalase and SOD mimetic activity tests revealed that the Ce-MGBs are able to act as mimetic materials for the two enzymes. Solid state analyses confirmed the presence of Hydroxyapatite over both MBGs samples: $80SiO_2$-15CaO-$5P_2O_5$ and $80SiO_2$-20CaO modified by 5.3% mol of CeO_2 and simultaneously these glasses maintain a good catalase activity. Moreover, the $80SiO_2$-15CaO-$5P_2O_5$ potential bioactive glasses showed SOD mimetic activity. These results highlight that it is possible to obtain a glass with both antioxidant and bioactivity properties. The future studies on these materials will be focused to test them in cellular cultures in order to verify if they are effective in protecting cells from the oxidative stress induced by ROS.

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O37 Zwitterionic Metallates of HEtSNS: Synthesis and Characterization of Bis- and Tris-Chelated Coordination Compounds

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The nucleophilic addition of aminophosphanes to alkyl- and aryl- isothiocyanate leads to the formation of the zwitterionic thioamidyl-phosphonium ($P^+C(S)N^-R$) functional group. Within this family of its compounds, $EtNHC(S)Ph_2PNPPh_2C(S)NEt$ (HEtSNS) can be prepared by reacting $Ph_2PNHPPh_2$ (dppa) in EtNCS as the reaction medium.[1]
In this work, we present a comparison between various metal complexes families and how this exceptionally flexible ligand adjust itself to best fit the metal requirement as a function of the metal centre and chemical conditions of the environment.[2,3]

There are four ways to achieve different HEtSNS coordination forms: i) varying its overall charge by changing its protonation state (H_2EtSNS^+, HEtSNS, $EtSNS^-$) either following the pH of the solution or via auto-protonation, ii) switching between S-N-S and N-N-N coordination, iii) interchanging between tris-chelating and bis-chelating bite, and iv) the possibility to bind more than one metal centre, forming systems with two metal ions per ligand molecule. The latter is done maintaining a one-to-one ligand-metal ratio in dimers or trimers, or binding other "free" metal ions, obtaining metal clusters.

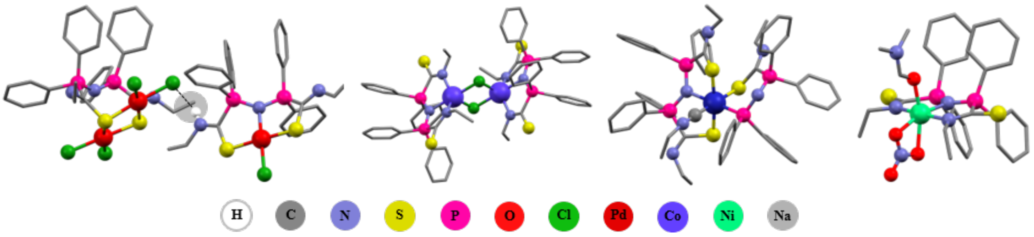

***Figure 1**: Four metal complexes with HEtSNS:* *[EtSNS($PdCl_2$)$_2$], [EtSNSCoCl]$_2$, [EtSNS EtSNP Co EtCN](PF_6)$_2$, [EtSNSNiNO_3DMF]*

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O38 Carbonaceous materials for the selective hydrogenation of HMF

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Biomass has recently attracted much attention as renewable carbon feedstock since it is abundant, widespread and inexpensive [1]. One of the most important products directly derived from lignocellulosic biomass is 5-hydroxymethylfurfural (HMF). Currently, a wide range of HMF derivatives are reported to be potentially suitable to use in several sector of chemical industries and as biofuels [2]. Among all these, the HMF hydrogenation products are of particular interest.

In this work, HMF hydrogenation was carried out with Ru nanoparticles supported on carbonaceous materials, specifically activated carbon (AC) and a wide range of functionalised carbon nanofibers (CNFs). The goal was to study the influence of the support on the reaction activity and selectivity. Special attention was given to three hydrogenation products (Figure 1a), namely 2,5-dimethylfuran (DMF), 2,5-dihydroxymethylfuran (DHMF) and alkoxymethyl furfurals (AMF). The results show a strong influence of the nature of the support, particularly on the selectivity (Figure 1b). When AC was used, the main product was DMF (75 %), with small presence of ethers and other products. The use of CNFs, on the other hand, resulted in a predominance of DHMF and AMF. In particular, with bare CNFs and oxygen-functionalised CNFs (CNFs-O), high amount of DHMF were produced (95 % and 80 % respectively), while with nitrogen-functionalised CNFs (CNFs-N) the predominant product was AMF (66 %). Finally, the phosphorous-functionalised CNFs (CNFs-P) showed poor selectivity, producing in similar amount both DHMF and AMF (47 % and 44 % respectively). All the catalysts were characterised with HRTEM, in order to obtain information on the Ru particle size and dispersion, and with XPS, in order to identify and quantify the surface functionalisation of each of the catalyst used, the degree of graphitisation of the carbon and the oxidation state of the Ru nanoparticles.

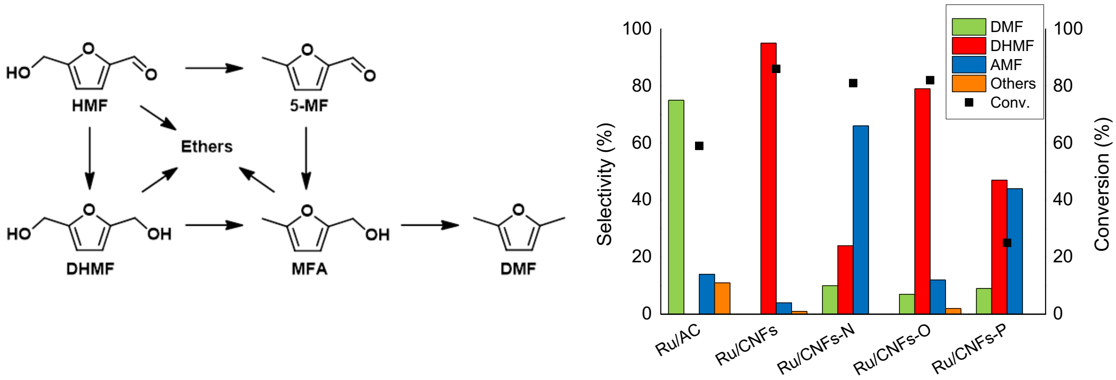

Figure 1. a) HMF hydrogenation scheme and b) catalytic results of the reaction at 150 °C and 20 bar of H_2.

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O39 Theoretical Insights on a biocompatible reduction route of graphene oxide by N-acetyl cysteine

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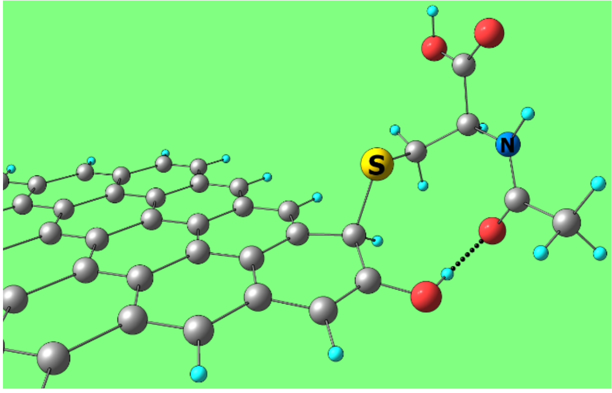
We propose here a novel method for the production and use of partially reduced graphene oxide (rGO) by means of a green biocompatible molecule, N-acetyl cysteine (NAC), which stays active at the rGO surface [1]. Such use of NAC has never been reported before.

We demonstrate by suitable chemical and biophysical techniques a partial and progressive reduction of graphene oxide (GO) at room temperature using NAC for different exposure times. NAC remains attached to the surface of rGO while retaining its activity, as shown with spectroscopic and microscopic techniques as well as with reliable tests of reactivity. This result is unprecedented in the field to the best of our present knowledge, and can be of advantage for drug delivery purposes, like brain delivery or pulmonary delivery, where anchored NAC can act as a radical scavenger. Given the widespread application of rGO in vivo, we foresee that this method of reduction can offer new possibilities for the graphene biomedical research field. Electrochemical reduction on the partially reduced GO has been carried out as a post-treatment [2,3], to better understand the GO reduction mechanism. Moreover, modelling of the graphene oxide reduction by NAC and the adhesion mechanism of NAC on rGO is proposed (Figure 1) and compared to the experimental findings. It was found that NAC can covalently graft on the edge of GO nanosheets as sulphide, partially retaining its reductant ability.



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O40 Electronic/Structural Aspects of the Functionalization of Phosphorene

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Phosphorene (P_n) 2D material is obtained by exfoliation of the layered black phosphorus.[1] Due to its fast reactivity with oxygen, P_n has to be protected or functionalized in order to increase its stability. The covalent functionalization is still scarcely addressed especially when transition metals are involved.[2] For this, we explored *in silico* models through solid state DFT calculations with the program CRYSTAL. The high density of the facial P atoms, with outpointing but not fully independent lone pairs, offers potential P_n reactivity with mono, bi- and three-functional acidic units, see Figure 1. In particular, we examined the reliability of the adducts between phosphorene and BH_3, I_2 or the ClAu(I) fragment.[3] The results have been compared with the established stereochemical and electronic features of the adducts with a phosphine or white phosphorus (P_4).[4] Other unsaturated Transition Metal fragments of the L_2M and L_3M type were chosen on the basis of the *isolobal analogy* concept[5] for combining neighbor P_n atoms with a single metal that carries multiple vacant lobes. Selected examples of new species will be highlighted.[3]

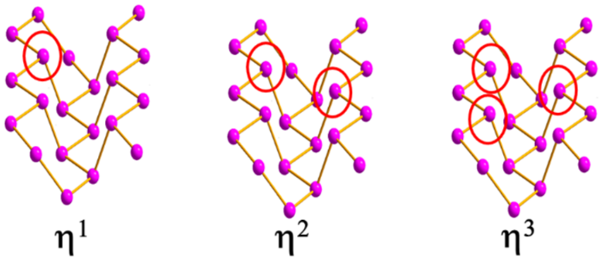

Fig.1. Different potential coordination sites of the P_n surface for acids or metal fragments.

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O41 Atmospheric pressure plasma processing of polyurethane sponges for oil-water separation

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Nowadays, functional materials for separation of oil-water mixtures attract growing interest in environmental remediation and wastewater treatment. In particular, over the last years, a wide range of absorbent materials with opposite wettability behavior towards water and oil has been successfully developed for this application.
The present work is focused on the optimization of unique atmospheric pressure non-equilibrium plasma processes [2] able to modify open-cell polyurethane sponges to obtain superhydrophobic/superoleophilic sorbents that can selectively absorb oil, while completely repelling water. The proposed approach involves two steps: first, an oxygen-containing dielectric barrier discharges (DBD) is employed to induce the nanotexturing of both the outer and inner surfaces of the sponge; then, in a second step an ethylene-containing DBD allows the deposition of a hydrocarbon polymer coating on the entire three-dimensional porous material. The sponges are characterized by X-ray photoelectron spectroscopy, scanning electron microscopy and mechanical tests before and after plasma processes. Contact angle measurements using both water and mineral oil as test liquids point out the simultaneous superhydrophobic/superoleophilic wetting properties of the plasma-treated PU sponges. Special attention is paid to the final performances of the plasma-treated sponges in terms of absorption capacity, separation selectivity and recyclability. Promising preliminary results are obtained using hydrocarbon solvents and mineral oil in absorption tests carried out over multiple reutilization cycles.

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O42 A new artificial reductase based on the D-Ala-D-Ala/Vancomycin supramolecular interaction and its applications in the enantioselective reduction of cyclic imines

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The widespread presence of metal ions in biological systems and the possibility to use nature-framed structures as ligands in transition metal complexes have prompted different research groups to investigate new artificial systems based on the combination of the reactive metals with different biological scaffolds[1]. Dalbapeptides[2], such as vancomycin, teicoplanin, ristocetin, are variously substituted heptapeptides whose antibiotic activity stems from their ability to tightly bind the D-Ala-D-Ala dimer of peptidoglycan precursor thus resulting in the inhibition of cell wall biosynthesis. This interaction is marked by such a low dissociation constant ($K_D = \sim 10^{-17}$ M) that it makes dalbapeptides an innovative and yet unexplored alternative to the classical biotin/(strept)avidin second coordination sphere system[3].

In this context, D-Ala-D-Ala functionalized diamines were employed as ligands for the synthesis of iridium(III) hybrid catalysts in presence of vancomycin and applied to the asymmetric transfer hydrogenation of cyclic imines, known for being important pharmaceutical precursors. An encouraging 48% (*S*) e.e. was obtained in the asymmetric reduction of the salsolidine precursor in sodium acetate 0.1 M buffer at pH 5. In the case of the most demanding isoquinoline substrates, an appreciable 71% (*S*) e.e. in the reduction of quinaldine[4].

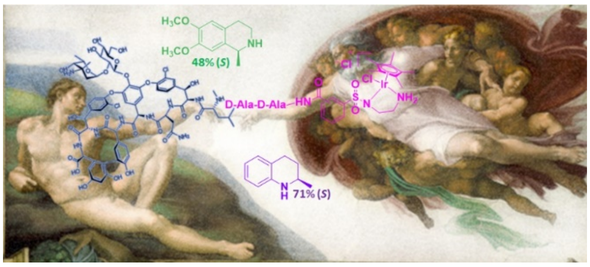

Figure 1*: Ir(III) imine reductase exploiting vancomycin as second coordination sphere*

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O43 Inorganic nanostructured templates for porphyrin J aggregates growth

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Organic- inorganic hybrid nanocomposites are widely studied in several scientific fields due to the emergence of new properties in terms of chemical and spectroscopic behavior, coming from the conjunction of different building blocks. In virtue of their interesting spectroscopic properties and their ability to form self-assembled structures, porphyrins represent interesting candidates as organic building blocks to realize hybrids nanocomposite materials. In particular, tetrakis (4-sulphonatophenyl) porphyrin ($TPPS_4$) is able to form self- assembled J- aggregates, with different shape and size, whose growth is closely related to the experimental conditions (i.e. pH, reactant concentrations, addition of salt and templating agents) [1-2]. In this work, the aggregation process of $TPPS_4$ in presence of different inorganic nanostructured materials is examined. As first example, we have chosen gold nanorods and clusters composed of ten metal atoms (Au_{10}). In both cases, formation of J aggregates can be revealed in solution at moderately acidic pH. Furthermore, on a glass surface the presence of Au_{10} and the acidity of the medium trigger the formation of a metallic self- assembled layer composed of gold nanoparticles and porphyrin aggregates. As second example in the class of 2D materials, carbon nanotubes functionalized with amine groups have been examined. The length of the spacer chains bearing the amino moiety plays an important role in porphyrin aggregation process. SPION nanoparticles have been also examined. All the investigated nanocomposites have been examined by detailed spectroscopic and morphologic characterization.

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O44 Synthesis, characterization and catalytic applications of transition metal nanoparticles embedded in polymeric nanoreactors.

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Metal nanoparticles (NPs) are largely investigated given their unique properties. With the recent advances in nanochemistry and particularly in the design of well-defined metal NPs, nanocatalysis is now recognized as a full and rich part of catalysis [1]. An efficient method for preparing well-controlled metal nanoparticles is the organometallic approach. Following this method, metal complexes are decomposed under mild conditions to release metal NPs either in the presence of polymers and/or ligands as stabilizing agents. In this work we present the use of recently developed triphenylphosphine (TPP) functionalized and hierarchically organized (amphiphilic core-shell) polymers, termed core cross-linked micelle (CCM), containing either a neutral [2] or a polycationic outer shell [3], as support for metal NPs, thus acting as a polymeric nanoreactor. TPP is confined in the polymer core (TPP@CCM, Fig.1). The TPP@CCMs were first loaded with complexes of Rh, Ru, Ir, Pt, Pd, Au and Ni and characterized by ^{31}P-NMR and DLS analyses, suggesting that PPh_3 coordinates all metals. All these polymer-supported complexes were reduced under H_2 at different temperature (depending on the metal) to give polymer stabilized metal NPs, which were employed as catalysts in acetophenone hydrogenation as a model reaction. The NP morphology was studied by TEM analyses before and after the catalytic applications.

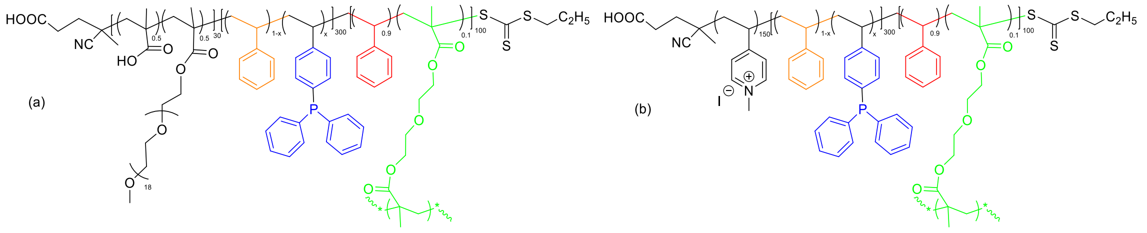

Figure 1: *Structure of core cross-linked micelle (TPP@CCM) with neutral (a) and polycationic (b) shell.*

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O45 Nature and Topology of Metal-Oxygen Binding Sites in Zeolite Materials

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Catalysis is the key enabling technology of the current chemical industry and heterogeneous (solid) catalysts dominate industrially relevant processes. Yet the exact nature and spatial arrangement of the active species is often ill-defined, if not completely unknown. Crucially, reactivity patterns often depend critically on the presence of paramagnetic species. Elucidating the role and influence of such species in catalytic processes is presently one of the most challenging endeavours from both an experimental and theoretical perspective and a limiting step in substituting noble metals with earth abundant elements.

There exist a number of spectroscopic techniques able to inform on the geometric and electronic structure of catalytic active sites, but either they yield information averaged over the bulk sample or lack description of the intimate features of chemical bonding, which include covalency, ionicity, electron and spin delocalization. In this contribution we show how the synergic combination of site-selective isotopic labelling with ^{17}O and advanced electron paramagnetic resonance (EPR) techniques can be used to derive site-specific structural and electronic models of industrially relevant zeolite materials [1]. Furthermore, we show how the most probable distance between neighbouring active sites, which falls in the nanometer range, can be inferred from pulsed EPR experiments with exquisite detail [2]. This is a non-trivial piece of information since currently there are no available spectroscopies capable to selectively report on the relative location of active sites in the nanometer range for disordered systems.

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O46 Light-activated Generation of NO and $SO_3^{\bullet-}$ from a Ruthenium Nitrosylsulfito Complex

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More than 150 years after C. Boedeker obtained the first nitrosylsulfito complex containing the nitrososulfonate ion $N(O)SO_3^-$ as a ligand,[1,2] the chemistry of such systems has not been fully studied. Moreover, very little is known about the biologically relevant $N(O)SO_3^-$ anion, which is unstable and generates reactive species.

This contribution reports the new nitrosylsulfito complex *trans*-$[Ru(isonicotinamide)(NH_3)_4(NOSO_3)]^+$ as a stable delivery agent of $N(O)SO_3^-$ via photoactivation.[3] Applying a hybrid approach based on experimental (UV-Vis, NMR, EPR, Transient Absorption Laser Flash Photolysis) and theoretical (DFT) data, we provide useful insights to understand the chemistry and the photochemistry of this kind of molecules. The results clarify the reaction pathways of $N(O)SO_3^-$ in biological conditions, where hydrolysis and attack by nucleophilic species are speculated. Furthermore, the photochemistry presented is the first ever described for a nitrosylsulphito complex, and demonstrates the production of two important radicals, $NO^\bullet$ and $SO_3^{\bullet-}$.

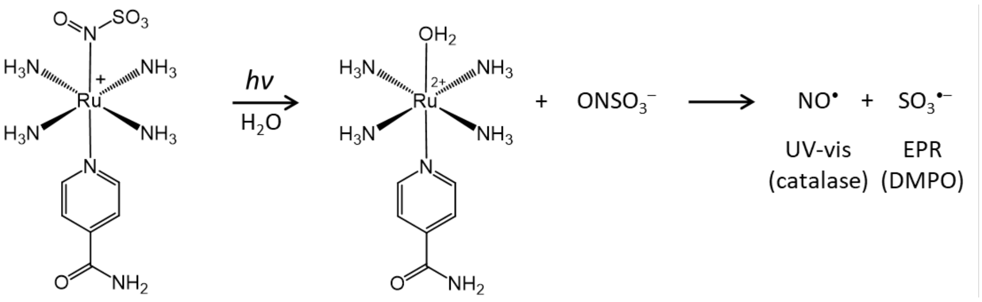

***Figure 1**: photochemical reaction pathway*

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O47 Supported gold nanoparticles catalysts for organic transformations

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Our research group has recently developed a convenient method for the anchoring of gold nanoparticles (AuNPs) on different oxide supports (SiO_2, Al_2O_3, TiO_2, Fe_3O_4) previously modified with a propynyl-carbamate organic functionality. The alkynyl-carbamate moieties anchored on the surface of the support are capable of straightforwardly reducing the gold precursor chloroauric acid ($HAuCl_4$) to afford Au/OS@Yne (OS = Oxide Support, Yne = organic functionalization), without the need of additional reducing or stabilising agents (Figure 1).[1,2]
After being thoroughly characterized by several complementary techniques (XPS, TEM, SSNMR, AAS etc.), the catalytic activity of these systems has been evaluated in the oxidation of alcohols and in the hydroamination of alkynes, both in batch and continuous-flow conditions.[1,3]

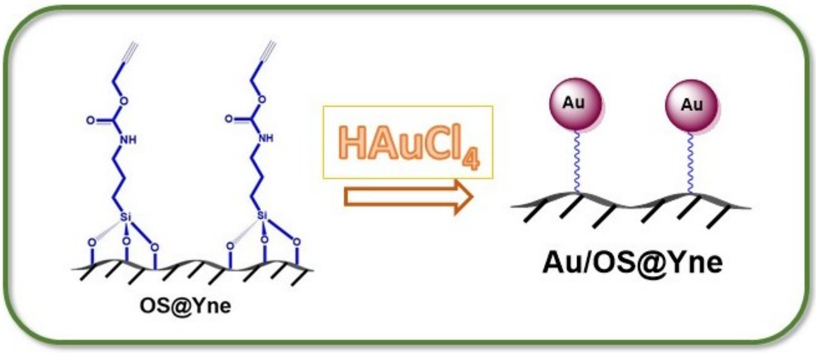

***Figure 1**: preparation of Au/OS@Yne.*

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O48 Flower-like Ce-Ti oxide systems for the CO preferential oxidation under solar light irradiation

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Nanomaterials have fascinated the scientific community in the recent years because of their unusual physico-chemical properties compared to those of their bulk counterparts. At the present time, the synthesis of large scale self-assembly starting by nanoscale building blocks into complex structures is a research hotspot. In fact it is expected that if the assembly mode of building units could be controlled and tuned to obtain a peculiar morphology [1], this could meet different needs and provide many different applications. Therefore, the design of systems with a controlled morphology and novel properties needs to be developed further.

The present work aims to investigate the photocatalytic behaviour of Au nanoparticles supported on CeO_2-TiO_2 matrices with a flower-like morphology in the CO preferential oxidation (photo CO-PROX), assessing not only the role of each component in the system and on the catalytic response, but also how a peculiar morphology can affect the photocatalysis. CeO_2 samples containing different TiO_2 loadings were synthesized by a surfactant-free and environmentally friendly slow co-precipitation method [2]. Au nanoparticles (1.0 wt% nominal loading) were deposited on the surface of the mixed oxides by deposition-precipitation.

Crystalline structure, morphological, textural and optical properties were investigated by several techniques. As shown by SEM microscopy, the samples appeared organized as an expanse of petals widely open around a sort of stem, in a hierarchical structure comparable to a microscale size flower. All the samples displayed a high specific surface area and a porous size distribution in the mesoporous region. HRTEM measurements revealed the presence of very small Au nanoparticles (2-4 nm average size) homogenously distributed on the surface of the supports. The flower-like Au/CeO_2-TiO_2 systems showed a morphology dependent behaviour in the preferential photo-oxidation of CO to CO_2 in excess of H_2 under simulated solar light irradiation at room temperature and atmospheric pressure, resulting much more active than samples with a non-organized structure.

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O49 Influence of Pd NPs size for bio-adipic acid production from muconic acid and sodium muconate

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Among the several subjects, the production of bulk chemicals from renewable sources is one of the great challenges that researchers are facing. Concerning this theme, adipic acid (AdA) production from wood biomass is one of the most important topics due to the large amount of AdA consumed and the market growth, in particular to produce polyamides (Nylon 6,6). Bio-AdA can be produced from t,t-muconic acid (t,t-MA), a metabolic intermediate of the catechol ortho-cleavage pathway.[1] Sodium muconate (Na-Muc) produced from bacteria can be converted to AdA with a heterogeneous hydrogenation chemical reaction.[2] 1% Pd/AC catalysts are well known for their high activity in hydrogenation reaction. Different catalysts were synthesized using sol-immobilization method[3], which allow to obtain small Pd NPs with controlled shape and size. The amount of stabilizer (polyvinyl alcohol) was varied to obtain catalyst with different Pd NPs size. Catalysts where characterized by BET, TEM and XPS analyses. All the catalysts show higher activity than 5% Pd/AC commercial catalyst and Na-Muc hydrogenation is more influenced by Pd NPs size, Pd(0)/Pd(II) ratio than t,t-MA hydrogenation.

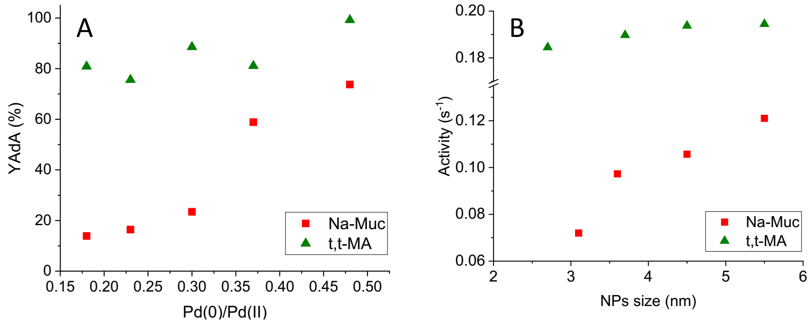

Figure 1*: influence of A)Pd(0)Pd(II) on AdA yield and B)NPs size on catalyst activity in Na-Muc and t,t-MA hydrogenation. [substrate]=00.142M, $P(H_2)$=1 bar, Na-Muc (t,t-MA)/Pd= 200/1 (mol/mol), T= 50°C*

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O50 Inhibition of amyloid aggregation by transition metal complexes

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A research field involving metal-based drugs as inhibitors of amyloid fibrils formation and toxicity is experiencing a great flowering. Transition metal complexes have tunable features, including oxidation, spin states and coordination geometries. All these features could trigger the reactivity of these compounds with amyloidogenic species with a consequent modulation of their aggregation pathways [1]. The metal complexes can undergo to ligand(s) substitutions with protein residue side chains, thus, the spatial arrangement of labile positions plays an important role. Here a series of square planar complexes of Pt(II), Pd (II) and Au(III) (figure 1) and octahedral compounds Ru(II) with O,S β-hydroxy dithiocinnamic esters, or 2-(2-pyridyl)benzimidazole as bidentate ligands were investigated employing different amyloid models [2]. Thioflavin T assay and CD data indicate that these compounds strongly inhibit the aggregation of investigated peptides exhibiting IC_{50} values in the micromolar range as confirmed by MS-analysis. Furthermore, several complexes demonstrated able to reduce amyloid cytotoxicity in human SH-SY5Y neuroblastoma cells.

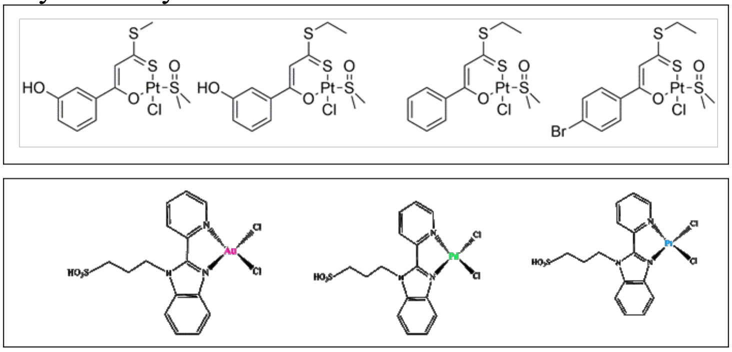

Figure 1 *Chemical structures of (upper panel) Pt(II) complexes bearing β-hydroxy dithiocinnamic ester, (lower panel) different metal ions with 2-(2-pyridyl)benzimidazole as ligands*

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O51 Plasma-assisted deposition of fungicide containing coatings for encapsulation and protection of maize seeds

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In the last decades, seed coated with proper chemical compounds have been widely used to reduce the impact of fungal diseases of the maize plants during the first growing stages. In particular, sowing coated maize seeds protects seedling plants in their early growth stages. In this work a fungicide containing multilayer has been deposited by plasma deposition. The polymeric layer deposited directly at the maize seed surface is obtained by feeding the discharge with C_2H_4 and CO_2. The outer polymeric layer is deposited from C_2H_4. All coatings have been deposited at 800 mTorr with 30 W of RF power. Prothioconazole was spray-deposited on the seeds, where the hydrophilic coating A was previously deposited, under shaking conditions, on 30 seeds placed in a Petri dish. Then the seeds were placed onto the ground electrode of the plasma reactor to be coated with an hydrophobic coatung. respectively. Control seeds exposed only to the fungicide solution are referred to as Pr.
Chemistry of the coatings was assessed by means of Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS). Static WCA measurements were performed to assess seed wettability. Water absorption of uncoated and coated maize seeds was evaluated. Absorption was tested for immersion time in the range 5-60 min.
All the layers have been well characterized; it was found that the water uptake of the seeds was not altered by the presence of the tri-layer, as well as the ability of the seeds to germinate, while the resistance of the plants to the infections by Fusarium graminearum was found greatly increased. The efficacy of the tri-layer in limiting fungal infection is most likely due to its capacity to both dose the leach in time of the fungicide compound in the soil around, and to act as barrier against the direct contact of the fungi with the seeds. Further studies clearly are needed to need to confirm this hypothesis, and certainly the structure of the tri-layer could be further optimized to better results.

O52 CARNOSINE AND TREHALOSE-CARNOSINE INTERPLAY IN THE ACTIVATION OF CREB FUNCTIONS AND COPPER HOMEOSTASIS

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Carnosine (β-alanyl-L-histidine) is a natural dipeptide widely distributed in mammalian tissues and presented at high concentrations (0.7–2.0mM) in the brain [1]. As reported previously, carnosine augmented the secretion and expression of various neurotrophic factors (for example, BDNF), leading to the induction of neurite growth in SY-SY5Y cells [2]. Moreover, carnosine glial release and neuronal utilization in CNS have been described [3]; carnosine intercepts the regulatory routes of Cu homeostasis in nervous cells and tissues. Cu dysregulation imply the oxidative stress, free-radical production and functional impairment leading to neurodegeneration. Barca et al showed that the extracellular carnosine exposure influenced intracellular Cu entry and affected the key Cu-sensing system (SP1 and CTR1) [4]. On this basis, carnosine, its derivate with trehalose and potential role of copper ions were investigated in the present study. First of all, we demonstrate that trehalose-carnosine crosses the cell membrane better than carnosine and its translocation does not depend on copper ions. On the next step, we analyzed a role of carnosine and its derivative in the modulation of CREB functions in the normal and in the copper ions deprivation conditions. Previously, it has been shown that carnosine and copper alone induce CREB phosphorylation [5, 6]. Here we found that 30 min of PC12 cells incubation with trehalose-carnosine stimulates CREB phosphorylation more than carnosine alone and the level of phospho-CREB depends on the presence of copper ions in the medium. To compare the influence of trehalose-carnosine and carnosine alone on copper homeostasis, a measure of the copper transporter CTR1 and transcriptional factor SP1 expression in culture of PC12 cells was carried out.

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O53 Assessing the Electrode-Electrolyte Compatibility in Solid-Oxide Cells with X-ray Microspectroscopy

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Solid-oxide cells (SOFC/SOEC) convert hydrogen to electrical energy and viceversa: due to the high operating temperature (>600 °C), they have high efficiency, tolerance to impurity in the fuel, and no need for noble metal catalysts. On the other hand, diffusion may occur at the interface between the different cell components during fabrication and operation. Using scanning X-ray microspectroscopy at the ID21 beamline of ESRF (Grenoble), we have investigated the effect of long-term thermal stress on the crystal chemistry of different cations at the interface between oxide cathodes (cobaltites, manganites, etc.) and electrolytes (Ca:$LaNbO_4$, Y:$BaCeO_3$, Sm:CeO_2). Our results [1-3] uncovered a wide variety of behaviors, including non-Fickian diffusive profiles for several different cations, segregation at the interface, and formation of layered structures. These are all expected to affect the long-term performance of the devices.

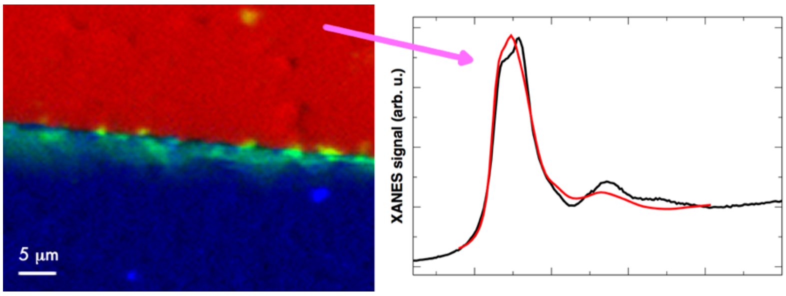

***Figure 1**: Elemental maps and a representative microXANES spectrum.*

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O54 Angiogenin bound to gold nanoparticles induces wound healing in the presence of copper ions

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Angiogenin (Ang) is one of the most potent angiogenic factors normally present in the human plasma. Ang is involved in most stages of the angiogenesis process and promotes the physiological course of healing of acute ulcers in the skin without scar formation. Copper is also an angiogenic factor in vivo and plays a key role in the synthesis and stabilization of skin proteins. There is a strict link between copper and Ang; copper ions increase the expression of Ang and modulates its intracellular localization in endothelial cells, affecting its angiogenic activity and signaling pathways activation. Ang is able to bind copper ions: the native form, present in vivo ("wild-type"-angiogenin, wt-Ang), which lacks the free amino terminal group, binds Cu^{2+} through His-114 and His-13, whereas the recombinant (r-Ang), mostly used in many literature reports, containing an extra methionine as first residue, binds the metal through the N-terminal amino group. The combined use of Ang and copper may stimulate angiogenesis acting against diversified categories of wounds such as acute and chronic. The use of the protein as therapeutic agent can be facilitated and made more effective by depositing it on nanoparticles, able to protect Ang from proteases. Gold nanoparticles (AuNPs) show antioxidant properties and can modulate angiogenic processes in the presence of copper ions. To facilitate the Ang functionalization on gold nanoparticles, a mutant protein (S28C-Ang) was expressed, with a cysteine instead of the serine at the residue 28, exploiting the high affinity binding to the metal surface by Au-S bonds. Spectroscopic characterization by UV-vis and CD show that S28C-Ang binds copper ions by using the same donor atoms of wt-Ang, confirming that mutation does not affect the functionality of the protein. The developed nanoparticles systems promoted fibroblasts migration and wound closure. Cell imaging by confocal microscopy evidenced synergic dynamic processes modulated by the different components (protein, gold nanoparticle, copper) at sub-cellular level (lysosomes-copper intracellular distribution). These results reveal a promising multifunctional platform as active wound healing and tissue regeneration agent.

O55 Plasma-assisted deposition of iron oxide thin films as photoanodes for water splitting

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A great effort is currently devoted to the development of materials and technologies suitable for the conversion of sunlight into chemical energy by photoelectrochemical water splitting. In this process, hydrogen is produced using sunlight and water, by means of a photoactive material that is able to simultaneously harvest solar light and perform water oxidation (photoanode) or reduction (photocathode) reaction. Hematite (α-Fe_2O_3) is considered a promising candidate as photoanode, thanks to its gap of 1.9-2.2 eV, allowing visible light absorption below 650 nm, large earth-abundance, low cost, nontoxicity, along with the stability in water and under illumination. [1]

In this contribution, we address the plasma-assisted deposition of iron oxide (FeO_x) thin films, from an iron target, in Ar/O_2 plasmas. Once deposited, FeO_x photoanodes were thermally annealed in oxygen. Film chemical composition and structure, as well as photoelectrochemical activity, were investigated as a function of the oxygen percent in the plasma feed mixture, and of the annealing temperature. Results show that deposition in pure argon plasma leads to nanostructured iron film with an oxide overlayer, fully converted to hematite (α-Fe_2O_3) upon thermal annealing and yielding the highest photocurrent density of 580 μAcm^{-2} at 1.23 V vs V_{RHE}. The addition of oxygen to the plasma feed mixture allows to grow directly hematite films but with a lower water oxidation activity (207 μAcm^{-2} at 1.23 V vs V_{RHE}). Strategies aimed at improving the photoelectrochemical activity of FeO_x films through the aid of additional plasma treatments will be finally presented and discussed.

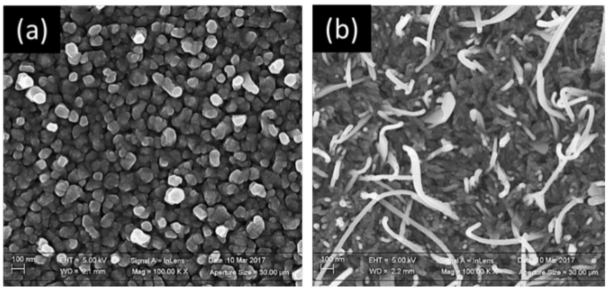

***Figure 1**: SEM images of FeO_x film deposited in Ar plasma before (a) and after (b) thermal annealing.*

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[1] I. Roger, M. A. Shipman, M. D. Symes, *Nature Reviews Chemistry* **2017**, 1, 0003.

O56 Dual-approach Pt^{II}-BODIPY conjugates: Theoretical Insights

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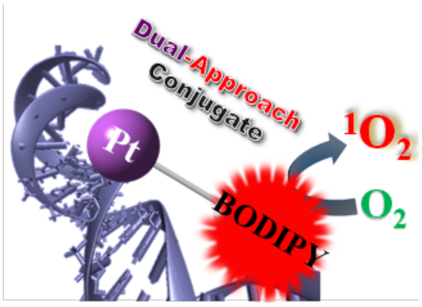
To afford a dual-approach anticancer treatment, the combination of a light-absorbing photosensitizer PS with a Pt^{II} ligand represents a very challenging strategy under investigation. [1]

A careful DFT and TDDFT investigation is herein presented on two different multi-target Pt^{II}-BODIPY conjugates, recently proposed [2], and on the two metal-free precursors, with the aim to explore the influence of the platinum moiety on the physico-chemical behaviour of the photosensitizer (PS) and to inspect in turn, the possible modulation of the hydrolysis rate of the Pt^{II}-ligand induced by the PS. The investigated photophysical properties for singlet and triplet states and the amplitude of the computed spin-orbit matrix elements reveal that the Pt-containing systems are able to enhance the cytotoxic $^1O_2$ production. The Pt^{II}-moiety instead, follows an activation mechanism similar to that previously found for cisplatin and its analogues already used in cancer therapy. [3]



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Acknowledgements: *This research was funded by Università della Calabria*

O57 VALORIZATION OF C5 POLYOLS BY DIRECT CARBOXYLATION TO FDCA: SYNTHESIS AND CHARACTERIZATION OF A KEY INTERMEDIATE AND ROLE OF CARBON DIOXIDE [1].

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Replacing fossil-C based plastics with those derived from renewable-C is one of the goals of the modern polymer industry. 2,5-Furan dicarboxylic acid (2,5-FDCA) is a candidate to substitute terephthalic acid as comonomer for polyesters. 2,5-FDCA is usually produced from C6 sugars. Carboxylation of 2-furancarboxylic acid (2-FCA) to 2,5-FDCA is an alternative synthetic approach to such monomer for polyethene furoate (PEF) preparation. In this work, several inorganic carbonates have been tested in the 2-FCA carboxylation in presence and absence of CO_2. A key copper intermediate has been synthesized and fully characterized that is able to increase the acidity and, thus, the reactivity of 5-H towards a carbonate species. Carboxylation occurs at 93 % yield in absence of CO_2. The role of metal salts and CO_2 were investigated. The conversion yield of 2-FCA into the dicarboxylic acid is related to the charge density on the metal cation, increasing with lower charge-density.

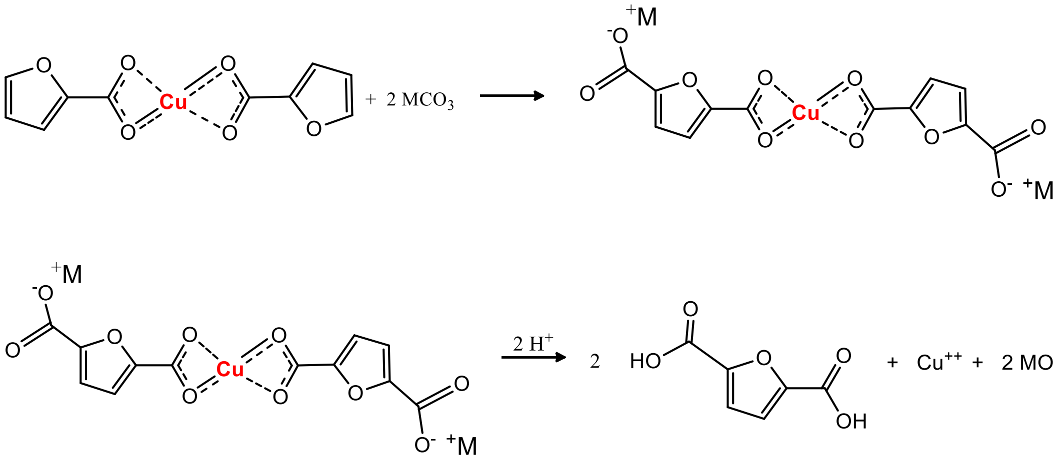

***Figure 1**: Carboxylation of 2-FCA using the copper-$(FC)_2$ as intermediate*

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Acknowledgements: *This research was funded by Prime Project, Regione Piemonte*

O58 Metal ion recruitment drives the folding mechanism and self-association propensity of high homologous proteins

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Using three isostructural proteins of the prokaryotic zinc finger family as model systems (Ml1$_{53\text{-}149}$ and Ros87 that bind a structural zinc ion and Ml4$_{52\text{-}151}$ that lacks it), our study is designed to contribute to the knowledge about the detailed mechanisms by which metal ions perturb proteins structure and function, folding mechanism and self-association propensities[1,2]. The prokaryotic zinc finger domain[3] shows a 58 amino acids *βββαα* globular fold that, stabilized by a 15 amino acids hydrophobic core, uses different combinations of amino acids to coordinate the structural metal ion when present[4]. We will discuss how the recruitment of the structural metal can modify the folding pathway of these relatively small domains, control conformational accessibility to aggregation-prone states and change aggregation kinetics. While these model domains have little direct disease-relevance, our results are certainly of broad general interest as many disease-relevant proteins bind metal ions, which could similarly influence their structures, folding pathways and aggregation.

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Acknowledgements: *This research was funded by the Italian Ministry of University and Research (MIUR): PRIN 20157WZM8A*

O59 Novel heterobimetallic complexes by coordination of *n*NHC/*tz*NHC heteroditopic carbene ligands

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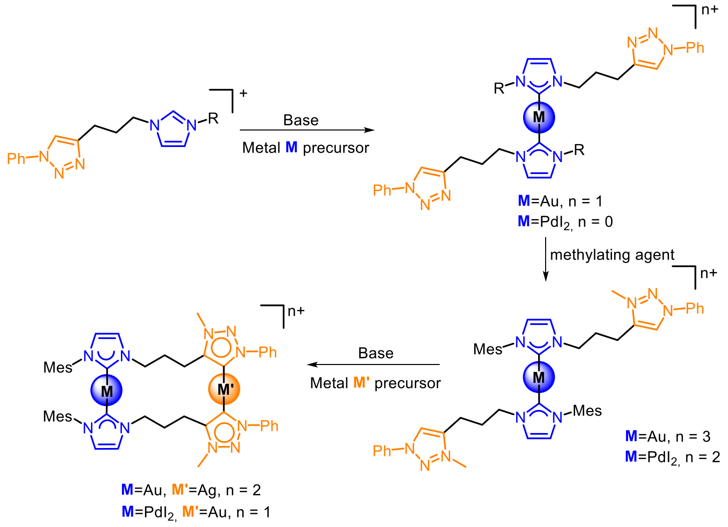
The synthesis of heterobimetallic complexes with N-heterocyclic carbene ligands remains a challenge, since the lacking of a general synthetic procedure.[1] We present here a possible approach in this regard which involves the use of heteroditopic bis(carbene) ligands, combining an imidazol-2-ylidene (*n*NHC) with a 1,2,3-triazol-5-ylidene (*tz*NHC) connected by an organic spacer. The optimized strategy to heterobimetallic complexes with this type of ligand involves a 3-step procedure: i) coordination to the first metal centre of the *n*NHC bearing a pendant 1,2,3-triazole ring, ii) alkylation of the triazole N-3 to give the triazolium salt, precursor of the *tz*NHC, iii) coordination of the *tz*NHC to the second metal centre. Following this procedure, Au(I)-Ag(I)[2] and Pd(II)-Au(I) complexes were isolated and characterized. Finally, the luminescence properties of the Au(I)-Ag(I) complex were also investigated and compared to those of the analogous homobimetallic Au(I)-Au(I) and Ag(I)-Ag(I) complexes.



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[1] see for example: a) J.A. Mata, F.E. Hahn, E. Peris, *Chem. Sci.* **2014**, *5*, 1723. b) M. Böhmer, G. Guisado-Barrios, F. Kampert, F. Roelfes, T.T.Y. Tan, E. Peris, F.E. Hahn, *Organometallics* **2019**, *38*, 2120.
[2] A. Longhi, M. Baron, M. Rancan, G. Bottaro, L. Armelao, P. Sgarbossa, C. Tubaro, *Molecules* **2019**, *24*, 2305.

O60 Multiscale Modeling of the Au(I) Chelating Motif in Protein *golB*

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Several bacterial species have evolutionary developed protein systems specialized in the control of intracellular gold ion concentration. In order to prevent the detrimental consequences that may be induced even at very low concentrations, bacteria such as *Salmonella enterica* and *Cupriavidus metallidurans* utilize Au-specific *merR*-type transcriptional regulators that detect these toxic ions and control the expression of specific resistance factors. Among these highly specialized proteins, *golB* has been investigated in depth, and X-ray structure of either apo and Au(I)-bound *golB* have been recently reported [1]. In our study, the binding of Au(I) at *golB* was investigated by means of multilevel computational approaches. Molecular dynamics simulations evidenced how conformations amenable for the Au(I) chelation through the Cys-XX-Cys motif on helix 1 are extensively sampled in the phase space of apo-*golB*. Hybrid QM/MM calculations on metal-bound structures of *golB* also allowed to characterize the most probable protonation state for gold binding motif and to assess the structural features mostly influencing the Au(I) coordination in this protein. Consistently with experimental evidences, we found that *golB* may control its Au(I) affinity, probably by conformational changes that affect the distance between Cys10 and Cys13, thus being able to switch on the Au(I) sequestration/release-prone states in response to external stimuli. The protein structure enveloping the metal binding motif favors the thiol-thiolate protonation state of Au(I)-*golB*, thus probably enhancing the binding selectivity for Au(I) compared to other cations.

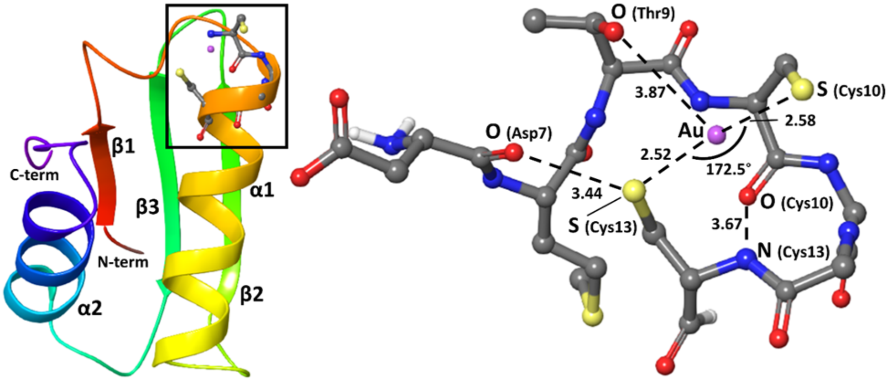

***Figure 1**: GolB protein chelating gold. X-ray structure: Ribbon representation of the whole protein on the left, metal-binding motif on the right. All distances are in angstroms, angles in degrees. The labels of atoms consist of the atom nomenclature followed by the residue name.*

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O61 Towards a Definition of Metal Organic NanoTube (MONT)

Andrea Ienco,[a] Annalisa Guerri[b] , Ferdinando Costantino[c] , Marco Taddei[d], Eugeny V. Alexandrov[e], Andrey A. Golov[e], Andrey V. Goltsev[e], Davide M. Proserpio[e,f]

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[d] Energy Safety Research Institute, Swansea University − Bay Campus, Fabian Way, Swansea, SA1 8EN, United Kingdom
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Metal-Organic Nanotubes (MONT) are a class of one dimension coordination polymers with open channels extended in one direction and assembled in crystalline frameworks with non-covalent interactions. [1] In recent years, some of us have reported the first two isoreticular MONTs assembled by Cu(II) metal atoms, diphosphinate and bipyridine ligands of different length. [2]
MONTs are a small subset of Metal Organic Frameworks. On the other side we found several ambiguities and confusions on the nature of MONT in the literature and we decide to give a clear definition of MONT based either on topology and on geometrical constraints. The latter are the smallest dimension of the internal cavity as well as the size of the windows in the lateral walls. With our definition, we extracted 35 "true" MONT from 28000 1D coordination polymers in the CSD database finding that most of the classified MONTs failed to fulfil our geometrical constraint.

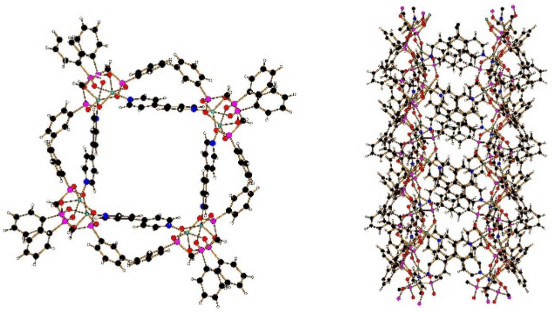

***Figure 1**:* An example of Metal Organic NanoTube.

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[1] P. Thanasekaran, T.-T. Luo, C.-H. Lee and K.-L. Lu, *J. Mater. Chem.*, **2011**, *21*, 1314.

[2] T. Bataille, F. Costantino, P. Lorenzo-Luis, S. Midollini, A. Orlandini. *Inorg. Chim. Acta*, **2008**, *361*, 327 . T. Bataille, S. Bracco, A. Comotti, F. Costantino, A. Guerri, A. Ienco, F. Marmottini. *CrystEngComm*, **2012**, *14*, 7170; M. Taddei, A. Ienco, F. Costantino, A. Guerri. *RSC Adv*, **2013**, *3*, 26177.

O62 *In vitro* and *In vivo* Properties of Pt(IV) Bifunctional Prodrugs Containing the 2-(2-Propynyl)octanoato Axial Ligand

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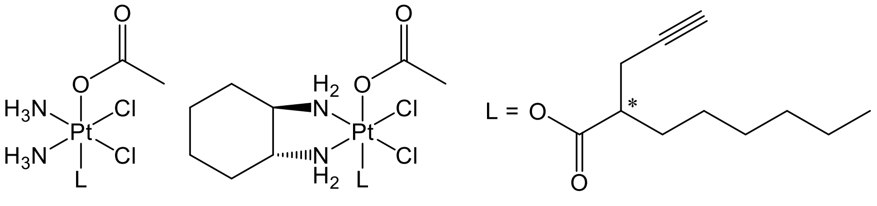
Pt(IV) complexes represent an interesting opportunity to design bifunctional anticancer molecules able to release simultaneously and selectively a Pt(II) active metabolite and a second drug in a sort of "*single-molecule combination therapy*". This assembly may reach intact its final target because of the relatively high inertness of Pt(IV) complexes, where they can be reduced to the corresponding cytotoxic Pt(II) metabolite, with the synchronized loss of the second drug molecules (*activation by reduction*), thanks to the hypoxic (and then reducing) intracellular milieu of tumor cells.

The second drug selected for this work is the very active inhibitor of histone deacetylase 2-(2-propynyl)octanoic acid, **POA**. The chemical and biological features of compounds **1** and **2** (Figure 1) will be shown. In general, the complexes were 1-2 orders of magnitude more active than their reference drugs cisplatin and oxaliplatin, respectively, depending on the sensitivity of the cancer cell lines. *In vivo*, orally administered **1** caused an impressive reduction of the mass (94%) in a model of solid tumor, whereas intraperitoneal cisplatin induced a tumor regression of 75% only. The time course of the body weight attested that cisplatin induced elevated anorexia, whereas treatment with **1** did not induce significant body weight loss. Also complex **2** showed higher decrease of the tumor mass than oxaliplatin, with negligible nephro- and hepatotoxicity, when administered intravenously. Importantly, the Pt(IV) treatment induced a remarkable tumor mass invasion by cytotoxic T lymphocytes, that specifically recognize and kill cancer cells, indicating a strong induction of immunogenic cell death [1].



1 **2** **POA**

Figure 1*: Sketch of (OC-6-44)-acetatodiamminedichlorido(2-(2-propynyl)octanoato),* ***1****, and (OC-6-44)-acetatodichlorido(cyclohexane-1R,2R-diamine)(2-(2-propynyl)octanoato)platinum(IV),* ***2****.*

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O63 Synthesis and investigation of new iridium complexes containing tetramethylcyclopentadienyl ligands variably substituted as potential catalysts for water oxidation

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Inspired by nature, artificial photosynthetic systems can be designed to store solar energy in chemical bonds by capturing sunlight, oxidise water to oxygen and reduce protons or other organic compounds. [1] The water oxidation half reaction is energy demanding and it is also complex from a molecular point of view, thus it is currently the bottleneck process for the development of an efficient water splitting device. [2] One of the strategies to overcome the high activation barriers consists in the involvement of transition metal species as catalysts. The more efficient catalytic systems to date are based on Ru [3] and Ir [4] molecular complexes.

We have synthesised iridium half-sandwich compounds bearing cyclopentadienyl ligands variably substituted (Figure 1) in order to study the influence of different substituting groups, in terms of electronic and steric properties, on the catalytic properties of the complexes. The newly prepared compounds have been characterized by analytical methods, and by IR and NMR spectroscopy; furthermore, their activity in water oxidation catalysis has been assessed.

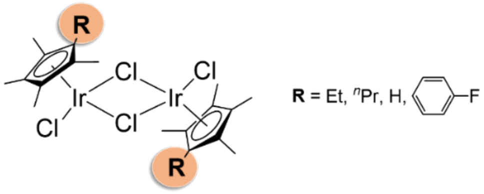

***Figure 1**. Newly prepared iridium complexes*

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[4] a) G. M. Rodriguez; A. Bucci; R. Hutchinson; G. Bellachioma; C. Zuccaccia; S. Giovagnoli; H. Idriss; A. Macchioni; *ACS Energy Lett.* **2017**, 2, 105−110; b) A. Bucci, S. Dunn, G. Bellachioma, G. M. Rodriguez, C. Zuccaccia, C. Nervi, A. Macchioni, *ACS Catal.* **2017**, *7*, 7788–7796; (c) M. Navarro, C. A. Smith, M. Li, S. Bernhard, M. Albrecht, *Chem. Eur. J.* **2018**, *24*, 6386–6398.

O64 Chiral ruthenium complexes: synthesis and evaluation of their anticancer activity

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Nowadays several metal compounds are widely used in medicine as therapeutic and diagnostic agents. Due to their versatile biochemical properties, ruthenium-based compounds have shown to be promising anti-cancer agents as alternative to cisplatin and its derivatives. [1] The aim of our work is to investigate the effects of new ruthenium(II) complexes of general formula [RuX(CO)(dppb)(phen)]X [X = acetate, pivalate, thioacetate; dppb = 1,4-bis(diphenylphosphino)butane; phen = 1,10-phenanthroline] [2] on two different types of anaplastic thyroid cancer cells, focusing our attention on the nature of the X group. Interestingly, these compounds are able to reach very low IC_{50} values after 72 h of incubation. In addition, the introduction of a chiral diphosphine, such as (*R*,*R*)- and (*S*,*S*)-Skewphos, leads to single enantiomers which show a marked difference in *in vitro* biological activity.

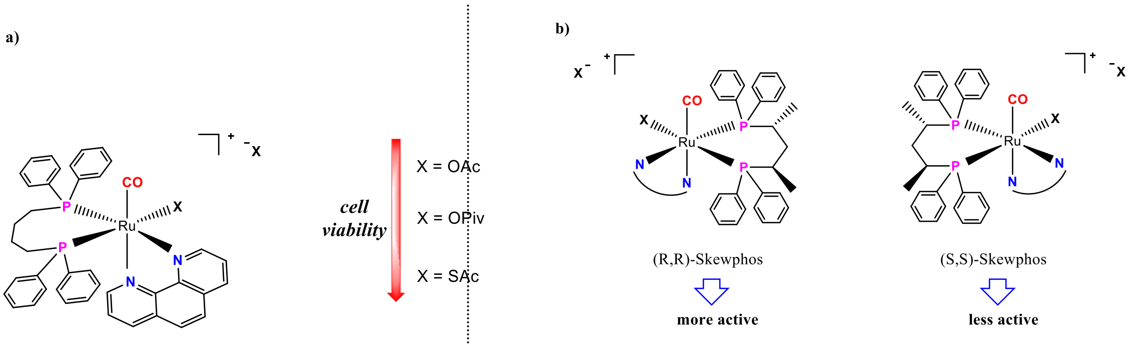

***Figure 1**: a) Ruthenium complexes with different X groups and their biological activity; b) Ruthenium enantiomers*

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[1] Leli Zeng, Pranav Gupta, Yanglu Chen, Enju Wang et al. *Chem. Soc. Rev.*, **2017**, *46*, 5681-6076
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Acknowledgements: *This research was funded by University of Udine*

O65 Ethereal Love: promoting ring-to-ring interaction in a [3]Rotaxane

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Rotaxanes are an example of mechanically interlocked molecules (MIMs) in which an axle is threaded through one or more macrocyclic rings. In such a way, the rings are confined to move along the axle and their de-threading is blocked by bulky groups at its extremities. Specific portions of the axle, called "stations", interact with the macrocycles through non-covalent bonds such as hydrogen bonds and hydrophobic or electrostatic interactions.[1] The weak nature of such interactions allows their use as switches or molecular machines controlled by pH variation, redox chemistry, or light irradiation.[2]

Reports about [n] rotaxanes comprising an even number of components are common in literature, and provided insight into shuttling or ring-station interaction switching mechanisms.[1] In contrast, examples of [n] rotaxanes comprising an odd number of components are rare, as are systems in which the number of rings is higher than the number of stations.[3] In this work we investigated the [3] rotaxane **1**, in which two benzyl ammonium stations can be deactivated by the addition of a base, providing the [3] rotaxane **2**, whose dibenzo-24-crown-8 rings are forced to share the remaining triazolium station (Figure 1).

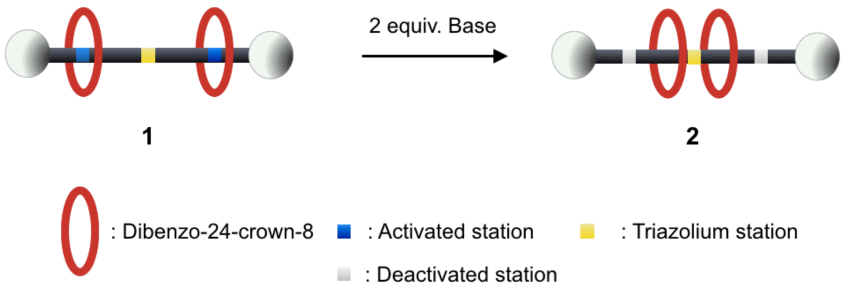

***Figure 1**. Enhanced ring-to-ring interaction in a [3] rotaxane induced by the deactivation of the ammonium stations.*

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[3] S. Lee, C.-H. Chen, A.H. Flood, *Nat. Chem.* **2013**, *5*, 704-710.

O66 Platinum-loaded, Selenium-doped hydroxyapatite for potential applications in bone tumors therapy

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Bone cancer has a high morbidity and is responsible for bone dyshomeostasis, which causes uncontrolled bone formation or resorption. Systemic antitumor chemotherapy not specific for bone cancer can lead to severe side-effects such as nephrotoxicity and neurotoxicity. A strategy to overcome the above-mentioned drawbacks consists in the delivery of cytostatic drugs from locally implanted bone substitute materials. Among bone substitute materials, hydroxyapatite (HA) is well known for its biocompatibility and capability to load a wide variety of compounds including therapeutic agents. In particular, we focused on the incorporation of SeO_3^{2-} into HA nanocrystals since this ion is endowed with intrinsic anticancer activity and SeHA nanocrystal (NPs) are used for systemic delivery of different anticancer drugs [1]. Bioactivity coupled with a higher selectivity to cancer cells may allow a targeted delivery with reduced systemic toxicity and enhanced chemotherapeutic efficacy. Since Pt-compounds are well known antitumor drugs (i.e. cisplatin, carboplatin, and oxaliplatin), we have designed platinum-loaded SeHA to achieve an enhanced therapeutic effect. A series of Se-doped HAs with different Se concentrations (i.e. different Se/P ratio) has been synthesized and characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR), Energy-Dispersive X-ray spectroscopy (EDS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and X-ray Photoelectron Spectroscopy (XPS). We have also studied the adsorption of a Pt-derivative with pyrophosphate, analog of phosphaplatins that are currently under Phase I clinical trials [2][Pt(Dihydrogen pyrophosphate)(cis-1,4-DACH)](Kiteplatin-pyrophosphate) on the SeHA. The release of Se and Pt from Pt loaded Se-HA *in vitro* was investigated at different pH values that mimic the pH of healthy tissues (pH 7.4) and tumor tissues (pH 6.5) in order to understand if a cytotoxic effect could be achieved at the doses of Pt and Se released from the NPs.

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1. Yifan Wang et al. "In Vitro and in Vivo Mechanism of Bone Tumor Inhibition by Selenium-Doped Bone Mineral Nanoparticles", *ACS Nano*, **2016**, *22*; 9927–9937.
2. www.phosplatin.com

O67 Electronic Properties of Electron-Deficient Zn(II) Porphyrins for HBr Splitting

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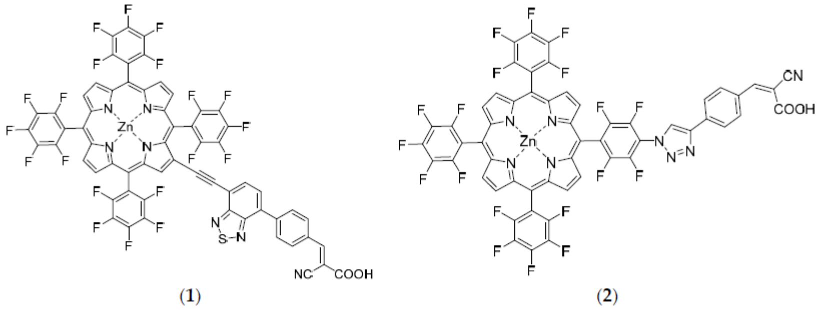
The present contribution deals with the investigation of the use of perfluorinated Zn(II) porphyrins in photoelectrosynthetic set-ups for HBr splitting, with the exploitation of two novel species (**1** and **2**, Figure 1), with structural features aimed at optimizing the charge separation in the resulting dye-sensitized photoanode. In particular, while maintaining the functionalization of the meso-position with perfluorophenyl groups, known to increase the oxidation potential of the resulting dyes,[1] we have introduced conjugated electron withdrawing linkers, terminating in cyanoacrylic groups for the anchoring to the semiconductor surface. Either □-pyrrolic or meso positions have been functionalized in order to evaluate their impact on the sensitization efficiency in terms of directionality of the charge injection from the excited state. In addition, porphyrin **1** displays also an additional acceptor benzothiadiazole (BTD) unit, which also contributes to the absorption of longer wavelengths. We have explored the electronic and spectroscopic properties of such species applied to the sensitization of n-type SnO_2 substrates, obtaining photoanodes capable to split HBr, with a better performance of porphyrin 1.



(1) (2)

***Figure 1**: porphyrins investigated in this contribution*

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[1] S. Berardi, S. Caramori, E. Benazzi, N. Zabini, A. Niorettini, A. Orbelli Biroli, M. Pizzotti, F. Tessore, G. Di Carlo, *Appl. Sci.* **2019**, *9,* 2739.

Acknowledgements: *This research was funded by Fondazione Cariplo Grant 2013-1766; UniMi PSR 2018 LINEA A Azione A–Giovani Ricercatori*

Posters

P1 Chromium (III) polypyridyl complexes for NUV photocatalysis

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Ruthenium and Iridium polypyridyl complexes are among the most investigated catalysts for NUV and visible light photocatalysis of common organic reactions involving the formation of C-C bonds [1]. These complexes have good photo-oxidising properties: when photoexcited, they can generate radical organic cations and thus start radical organic reactions. Recently, Ru(II) and Ir(III) complexes with one 2,2'-bipyridine-5,5'-dicarboxylic acid as anchorable ligand have been efficiently incorporated in dicarboxylate-based metal-organic frameworks, such as UiO-67, yielding a heterogeneous photocatalyst [2]. The main disadvantage of these complexes is the high cost of the metal; chromium(III) polypyridyl complexes offer an interesting alternative, both for their improved photophysical properties and for the lower cost of the metal [3]. However, since chromium(III) is particularly inert towards ligand substitution, it was necessary to explore its coordination chemistry with different ligands, such as substituted bipyridines and phenantrolines. With the aim of immobilising the photocatalyst into a metal-organic framework, bipyridines structurally similar to UiO-67 dicarboxylate linker were used too. We report the synthesis of two homoleptic and four heteroleptic chromium(III) complexes with different polypyridyl ligands. All the products were characterised with FT-IR, Raman and UV-Visible spectroscopy, as well as mass spectrometry. Photocatalytic trials showed that the complexes were able to photocatalyse in homogeneous phase the dimerisation of 1,3-cyclohexadiene with good conversion and selectivity under NUV light. These results assess the effectiveness of chromium(III) complexes in organic photocatalysis, opening a new possibilities for cheaper and more accessible synthetic organic reactions, with respect to the traditional Ru(II) and Ir(III) photocatalysts.

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P2 Atmospheric pressure He/O_2 plasma treatment of polyurethane foams and heavy metal ions adsorption from water

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Non-equilibrium plasmas are suitable for the surface processing of several materials (also thermal sensitive organic polymers) since they do not modify their bulk structure and properties [1]. In the last years, atmospheric pressure non-equilibrium plasmas have attracted growing interest in this applicative field thanks to the utilization of easy-to-handle apparatuses, the absence of complex and expensive vacuum equipments and their compatibility with continuous production lines. Different approaches can be used to generate these plasmas; among them, dielectric barrier discharges (DBDs) are probably the most common utilized [2,3]. Due to their operating conditions, DBDs allow the ignition of the discharge also inside small cavities allowing the modification of the inner and outer surfaces of three-dimensional (3D) porous substrates [4].

This contribution focuses on the treatment of 3D commercial open-cell polyurethane (PU) foams with atmospheric pressure DBDs fed by helium and oxygen mixtures, in order to functionalize the entire foams with oxygen containing groups. Plasma treatments were carried out using a home-built atmospheric pressure DBD reactor with parallel plate electrode configuration. The ignition of the discharge outside and inside the PU foam was observed (Figure 1). The X-ray Photoelectron Spectroscopy characterization showed that a uniform treatment with an efficient functionalization with oxygenated chemical groups was achieved.

The possible application of functionalized foams for the adsorption of heavy metal ions from water solution was investigated by means of Anodic Stripping Voltammetry. Cadmium ion was mainly used as metal probe. Experimental results evidenced that the adsorption capacity of PU foams was significantly increased after plasma processes.

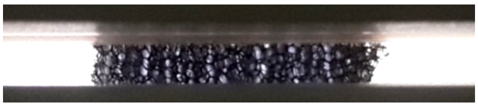

Figure 1. *Photograph of the DBD during the plasma treatment of a PU foam*

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[1] R.d'Agostino, P.Favia, F.Fracassi, "Plasma Processing of Polymers", **1996**, Kluwer Academic Publishers, Dordrecht/Boston/London
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P3 Study of the Molecular and Electronic Structure of Copper Coordination Compounds Conjugated to Gold Nanoparticles as Innovative Anticancer Drugs

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Copper complexes are coming out as metal-based drugs candidates for the treatment of cancer, due to their wide structural variability, biologically accessible redox properties and bioavailability. Recently, in our quest to find suitable ligands in the design of copper-based anticancer agents, we focused our attention on the synthesis of copper complexes of bis(azol-1-yl)carboxylate ligands functionalized with biomolecules (Fig. 1a). In addition, Cu(II) complexes of alkyl bis(pyrazol-1-yl)acetate ligands (Fig. 1b) have been investigated for the development of a new and more efficient promoter for the Kharasch-Sosnovsky reaction to oxidize alkenes in allyl position. Since such coordination compounds have low solubility in aqueous medium, it is necessary to design a strategic approach allowing for drug delivery. By conjugating the copper complexes with hydrophilic gold nanoparticles, it is possible to improve their solubility and stability in water, increasing their bioavailability. Moreover, these drug delivery systems allow the investigation of a slow and controlled release of copper complexes [1].

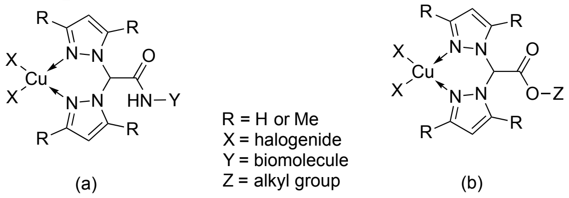

Figure 1. *Molecular structure of Copper(II) complexes*

In this context, we carried out a spectroscopic investigation of the molecular, electronic structure and coordination geometry of a selection of Cu(II)-coordination compounds, by means of complementary X-ray techniques induced by Synchrotron Radiation: the molecular and electronic structure were probed by means of SR-XPS and NEXAFS, the oxidation state and the local coordination chemistry of the metal ion were assessed by Cu K-edge XAFS analysed in the near edge (XANES) and extended (EXAFS) regions.

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Acknowledgements: The Grant of Excellence Departments, MIUR (ARTICOLO 1, COMMI 314 – 337 LEGGE 232/2016), is gratefully acknowledged by Roma Tre authors.

P4 Iron and ruthenium glyco-conjugated porphyrins: eco-friendly catalytic systems for three-membered rings synthesis

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The synthesis of three-membered ring compounds, such as cyclopropanes and aziridines, is an important topic in organic chemistry due to their use as building blocks and biological and/or pharmaceutical activity [1]. Therefore, the development of sustainable synthetic procedure for obtaining these products continues to be a significant challenge.

Even if carbohydrate porphyrin conjugates gained much attention in photodynamic therapy (PDT), [2] their potential use in catalysis has been less investigated.

Thus, our interest was focused on the synthesis and catalytic activity of different iron and ruthenium glycosylated porphyrins (Figure 1) in promoting cyclopropanations and aziridinations of styrenes. The use of diazo-compounds and organic azides, as precursors of carbene [CRR'] and nitrene [NR''] functionalities respectively, enhances the atom-efficiency of the process due to the formation of N_2 as the only stoichiometric by-product (Figure 2). The number and location of the carbohydrate units onto the porphyrin ring were rationalized up to reach excellent diasteroselectivities. To the best of our knowledge this is the first example of metal glycosylated porphyrins able in performing a shape selectivity, where only reactants of the opportune size are allowed to react over the active catalytic site to yield desired compounds.

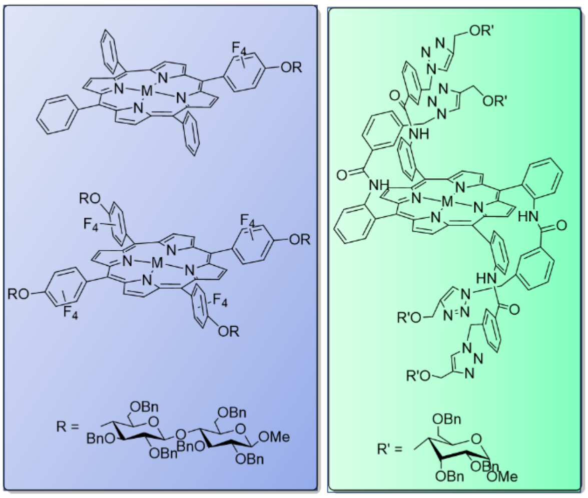

***Figure 1**: Glycoporphyrin complexes*

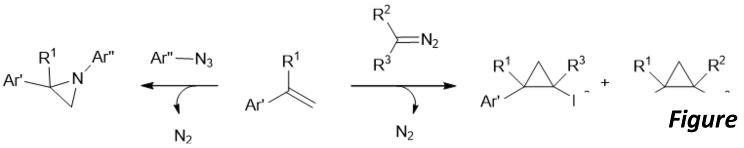

***Figure 2**: Aziridination and cyclopropanation reactions catalysed by glycoporphyrins complexes*

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[2] a) S. Singh, A. Aggarwal, N. V. S. D. K. Bhupathiraju, G. Arianna, K. Tiwari, C. M. Drain, *Chem. Rev.*, **2015**, 115, 10261−10306; b) C. Moylan, E. M. Scanlan, M. O. Senge, *Curr. Med. Chem.*, **2015**, 22, 2238-2348

P5 Hydroxyapatite coatings interaction with a self-assembling peptide: a XPS, FTIR and NEXAFS study

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Titanium and its alloys, such as Ti6Al4V, are well-known biocompatible materials widely used in dental and orthopedic prostheses [1]. In order to improve biocompatibility, hydroxyapatite (HAP) coatings can promote bone growth on the interface between an implant and the extracellular matrix due to their good bioactive ability.

In this framework, we studied the surface of HAP coatings deposited by magnetron sputtering on the Ti6Al4V alloy. The HAP surface was furtherly functionalized by adsorption of a self-assembling peptide, consisting of a regular alternation of polar and apolar residues and capable to generate extended ordered structures by self-assembling from water solutions.

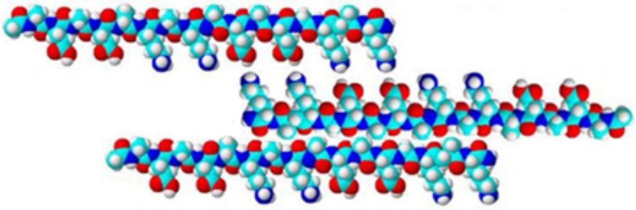

***Figure 1**: Self-assembling peptide structure*

Samples were analyzed by XPS, FTIR and NEXAFS spectroscopies in order to determine the amount of adsorbed peptide, the peptide structure stability and the molecular order and orientation of the peptide overlayer on the HAP coatings.

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P6 Hybrid Architectures as Active Light Harvesting Systems

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[b]University of Rome La Sapienza, 00185-Rome, Italy
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During the last decade, many research groups explored the possibility to use the sunlight as a renewable energy source by using artificial molecular networks able to mimic the natural photosynthetic process. These networks can be obtained from the combination of different moieties, the Donor (ferrocene), the photoactive compound (porphyrin) and the Acceptor (carbon materials: Carbon Spheres-CSs, Graphene Nanoplates-GNP and Fullerene-C60) connected to each other through "molecular wires" of variable lengths.[1,2] GNP are synthesized from a scalable and stable fabrication method, relying upon the microwave irradiation. CSs are obtained from a low-cost floating catalyst CVD process.[3] TEM and SEM microscopy help understanding the inner and outer morphology of CSs and the surface area or the layers number in GNP. Steady-state fluorescence studies together with Raman and XPS measurements helped investigating the chemical and physical properties of the porphyrin ring in the new adducts. In order to localize the preferential binding sites, a mapping characterization has been carried out on the sample through the Raman imaging. Preliminary studies of transient absorption spectroscopy were performed to investigate the possible electron-transfer events in the hybrid materials, while electrochemical studies to underline the interactions between the different parts of the new adducts.

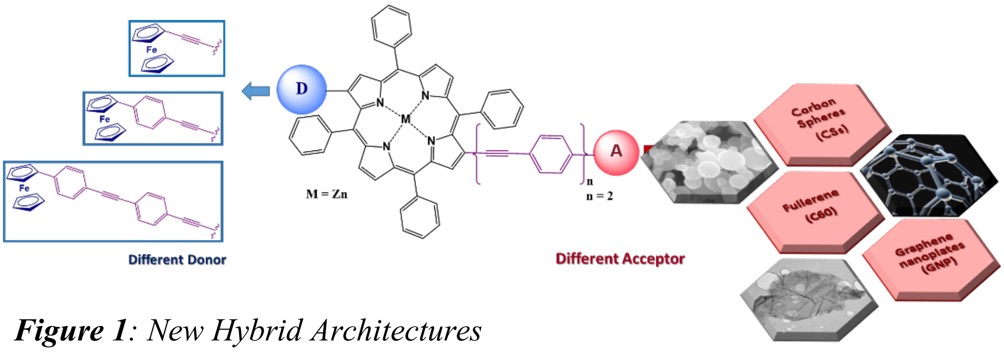

***Figure 1**: New Hybrid Architectures*

[1] F. Limosani, F. Possanza, E. Ciotta, F. Pepi, C. Salvitti, P. Tagliatesta, R. Pizzoferrato *J. Porphyrins Phthalocyanines* **2017**, *21*, 364-370.
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[3] M. Scarselli et al, Adv. Mater. Interf. 2018, 1800070 (1-10).

P7 On the origin of the multi-site behavior of Cp^{Alkyl}Hf(IV)-catalysts for olefin polymerization

Leonardo Tensi,[a] Cristiano Zuccaccia,[a] Roger L. Kuhlman,[b] Anthony P. Gies,[c] Alceo Macchioni,[a]

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Olefin polymerizations catalyzed by molecular catalysts are commonly considered single-site processes. However, even simple metallocene[1] and post-metallocene[2] precursors often generate multimodal polymer compositions, typical of multi-site processes. A relevant example, studied by us, is olefin polymerization catalyzed by $(Cp^{Pr})_2HfMe_2$. NMR investigations show that, when activated with a proper co-catalyst, $(Cp^{Pr})_2HfMe_2$ undergoes a rapid intramolecular C-H activation of the propyl moiety leading to a metallacyclic complex. Moreover, the resulting metallacycle is an effective 1-hexene polymerization catalyst with activity comparable to that of the non-metalated precursor. *Ad hoc* polymerizations allow the isolation of polymers containing $(Cp^{CH2-CH2-CR3})_2HfCl_2$ (R = H or polymeryl) fragments,[3,4] derived from the irreversible incorporation of polymer chains onto the cyclopentadienyl ligand substituent(s), which were also active species for olefin polymerization, producing polymers with different features and, possibly, being responsible for the observed multisite behavior (Figure 1).

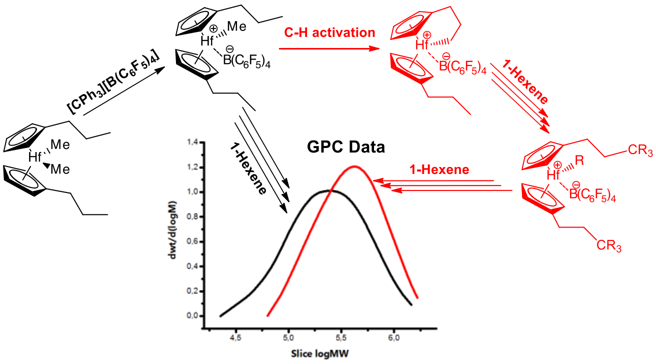

***Figure 1**: Relationship between catalyst speciation and multi-site behaviour of 1-hexene polymerization.*

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Acknowledgements: This research was funded by CIRCC and Univation Technologies LLC.

P8 Highly Selective Pb(II) Recognition in Metalloregulatory Protein *pbrR691*: Multilevel Computational Study

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The Pb(II) transcription factor *pbrR691*, a member of the *merR* family of metalloregulatory proteins, was recently discovered in *Ralstonia metallidurans CH34*. This protein is the only known metalloprotein in nature that is activated specifically by Pb(II). This protein operates as a homodimer *(pbrR)*$_2$ in solution and tightly controls the *pbr* transcription operon, which has integrated functions in the uptake, efflux, and accumulation of Pb(II). This metalloregulatory protein detects Pb(II) with at least 1000-fold selectivity over other metal ions, such as Cu(II), Zn(II), Co(II), Hg(II), and Cd(II) [1]. The binding of Pb(II) at *(pbrR)*$_2$ was investigated by means of multilevel computational approaches. Molecular dynamics simulations studied the conformations amenable for the Pb(II) chelation through the *(Cys)*$_3$ motif. Hybrid QM/MM calculations on metal-bound structures of *pbrR* permitted to identify the most probable protonation state and to gauge the structural features that influence predominantly the Pb(II) coordination in this protein. In agreement with experimental data [1], we concluded that Pb(II) displays a stereochemically active lone electron pair that is not involved in bonding to ligands, thus adopting a hemidirected geometry with all ligands clustered on one side of the metal. We were able to show that it is the protein folding that imposes such a unique geometry, that allows *(pbrR)*$_2$ to selectively chelate Pb(II) and ostracize other soft metal ions. In this scenario other metal ions would remain in solution and circumvent these high energetic penalties to enter the metal binding site in *(pbrR)*$_2$.

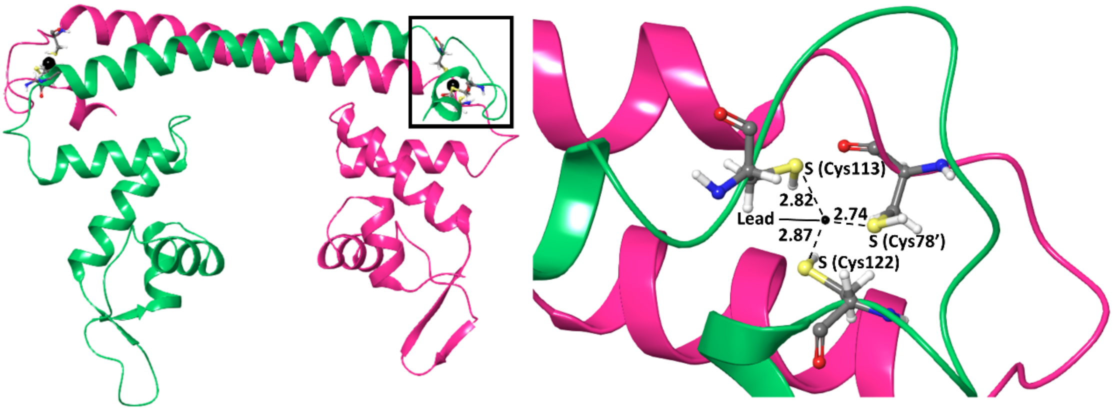

Figure 1*: PbrR homodimer chelating lead. X-ray structure: Ribbon representation of the whole protein on the left, metal-binding motif (Cys)*$_3$ *on the right. All distances are in angstroms.*

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[1] P. Chen et al., *Angew. Chem., Int. Ed.* **2005**, *44*, 2715–2719.

P9 Novel Multifunctional Magnetic Inorganic Composites: Synthesis and Characterization

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We report the preparation of a series of new magnetic inorganic composites (MICs) with tuneable magnetic and mechanical properties. In the field of power inductive components and inductive heating, they could transfer energy with high robustness and excellent performances. Moreover, they may mitigate electromagnetic interference (EMI) in the LF and MF band. The MICs have been prepared using an alkaline or acidic activation process carried out in the presence of commercial magnetic micrometric particles made of anisotropic and isotropic Sr-ferrite. Three different matrices have been prepared, varying the type of activator, slag addition, water content, and aggregates.

Sample	GL55	GL55B	GL56	GL21F	GL21G
Matrix	G1		G2	G3	
Magnetic Nanoparticles (MNPs)	Sr-Ferrite anisotropic	Sr-Ferrite isotropic	Sr-Ferrite isotropic	Sr-Ferrite isotropic	Sr-Ferrite anisotropic
Nominal concentration	11.2	10.2	8.9	5.9	5.9

Figure 1: *The nominal relative concentration of magnetic particles carried out at 300 K*

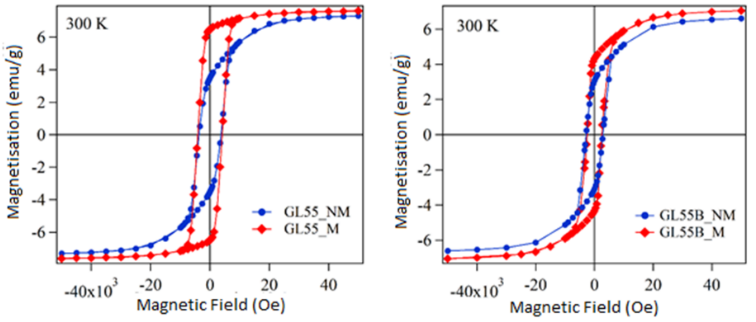

Figure 2: *The effect of the magnetization process during the solidification of the samples.*

[1] S. Kalia, S. Kango, A. Kumar, Y. Haldorai, B. Kumari, R. Kumar - Colloid and Polymer Science 292 (2014) 2025
[2] J. Park, J. Joo, S.G. Kwon, Y. Jang, T. Hyeon - Angewandte Chemie Int. Ed. 46 (2007) 4630

Acknowledgements: *This research was funded by 2017 BIRD Project.*

P10 Gold Nanorods: Synthesis and Structural Characterizations in view of Biomedical Applications

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Currently, nanotechnology plays a crucial role biomedicine, both in diagnosis and therapy, and several kinds of nanoparticles have received significant attention in these fields. In particular, gold nanorods (AuNRs) have advantageous properties including multifunctionality and multivalency effects, as schematized in figure 1, useful to be combined in theranostics.[1,2] In fact, AuNRs show modulable surface chemistry and little or no cytotoxicity in various cell/animal models.[2,3] Moreover, they can be conjugated with targeting ligands or imaging agents, for improved affinity (avidity) and targeting efficiency.[4-5] In this framework, new functionalized AuNRs, high hydrophilic, biocompatible and with size suitables for theranostic applications,[6] were presented together with their UV-Vis, FTIR, and SR-XPS characterizations.

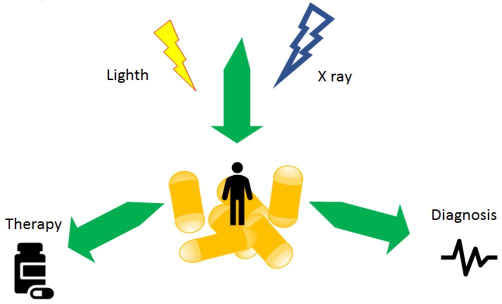

Figure 1*: Scheme of AuNRs multifunctionality and multivalency in therapy and diagnosis*

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[2] J. K. Patra, et al., *J. Nanobiotechnology*, **2018**, *16*, 71
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Acknowledgements: *The Grant of Excellence Departments, MIUR (ARTICOLO 1, COMMI 314 – 337 LEGGE 232/2016), is gratefully acknowledged by authors of Roma Tre University.*

P11 Glyconjugated carbene Pt(IV) complexes: synthesis, characterization and cytotoxic activity.

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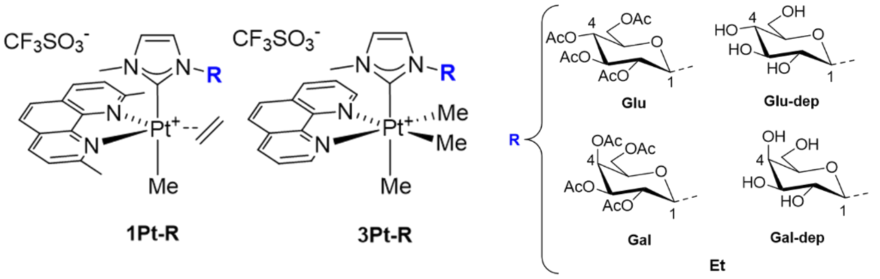
The efficacy of Pt(II) anticancer agents is often limited by remarkable toxicity and resistance.[1] It is also well known that tumor cells significantly increase carbohydrate uptake to maintain the cellular homeostasis and ensure proliferation (Warburg effect). In this context glycoconjugates Pt-complexes promise to improve the selectivity exploiting the selective recognition of glycosyl fragment by tumor cells.[2] To further enhance the performance, Pt(IV) complexes can be selected as 'prodrugs', which undergo reduction to the active Pt(II) species in the cellular environment.[3] This offers therapeutic advantages since Pt(IV) agents are more resistant to ligands substitution compared to their Pt(II) counterparts, thus limiting undesired side reactions in physiological media and lowering toxic side effects.

On these basis, the present work is focused on the design of new Pt(IV) complexes containing glycoconjugated *N*-heterocyclic carbene residues of general type **3Pt-R**.



The evaluation of their biological activity and the interaction with biological targets (DNA and model proteins) offered the possibility to have a direct comparison with the analogue Pt(II) carbene complexes **1Pt-R** studied in a parallel work.[4]

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[2] A. Pettenuzzo, R. Pigot and L. Ronconi, *Metallodrugs*, **2016**,*1*, 36-61

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P12 Highly Fluorescent Boron Complexes of Imidazo[1,5-*a*]pyridine Phenols

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Imidazo[1,5-*a*]pyridines constitute a very interesting class of heterocyclic compounds whose photochemical properties have been widely explored; their most relevant features are large Stokes shift, high quantum yields and a wide range of emission depending on their functionalization. Furthermore, there are numerous publications on luminescent transition metal compounds or fabrication of Organic Light Emitting Diodes (OLEDs) based on imidazo[1,5-*a*]pyridines. We also reported on fluorescent zinc(II)[1] or silver(II)[2] complexes with these ligands, while more recently we investigated the emissive properties of different tetrahydro(imidazo[1,5-a]pyrid-3-yl)phenols.[3] Herein we discuss the relevant fluorescent behavior of a series of boron difluoride functionalized imidazo[1,5-*a*]pyridine phenols (Figure 1), where the introduction of the BF_2 moiety dramatically increased the emissive performances, highly modulable by the electronic features of the substituent R in the phenolic residue.

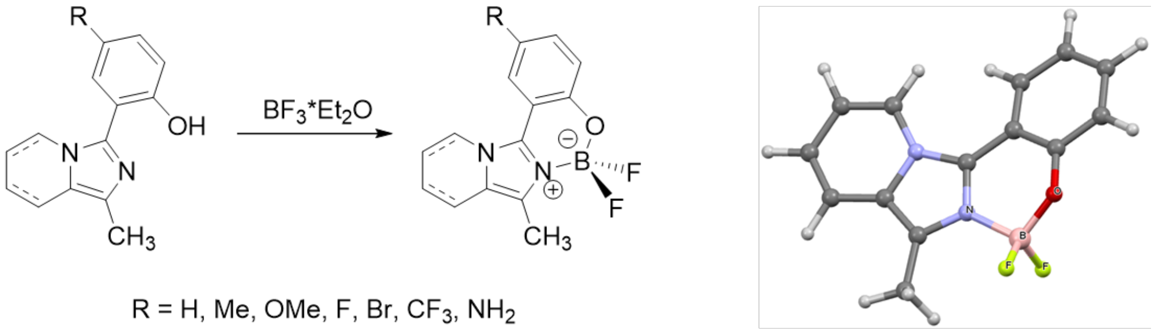

Figure 1: *Boron complexes of imidazo[1,5-a]pyridine phenols object of this study.*

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[1] a) G.A. Ardizzoia, S. Brenna, S. Durini, B. Therrien, M. Veronelli, *Eur. J. Inorg. Chem.* **2014**, 4310-4319; b) G.A. Ardizzoia, S. Brenna, S. Durini, B. Therrien, *Polyhedron* **2015**, *90*, 214-220; c) G.A. Ardizzoia, G. Colombo, B. Therrien, S. Brenna, *Eur. J. Inorg. Chem.* **2019**, 1825-1831.
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[3] A. Marchesi, S. Brenna, G.A. Ardizzoia, *Dyes and Pigments* **2019**, *161*, 457-463.

Acknowledgements: *This research was partially funded by University of Insubria and Fondazione Banca del Monte di Lombardia (FBML).*

P13 Oxaliplatin analogs bearing the ligand *trans*-1,2-diamine-4-cyclohexene.

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Oxaliplatin, 1*R*,2*R*-diaminocyclohexane(oxalato)platinum(II), is still one of the most successful cisplatin analogues used in the clinics. It was firstly launched in France in 1996 for the treatment of colon carcinoma and then adopted all over Europe in 1999 and in USA in 2002. This third-generation platinum drug contains the diaminocyclohexane (DACH) ligand and some analogs, containing DACH isomers, have been synthesized and tested. One of them, [$PtCl_2$(*cis*-1,4-DACH)] (Kiteplatin), has shown significant effectiveness in overcoming cisplatin and oxaliplatin resistance.[1] Other derivatives, such as those containing pure enantiomers of 4-methyl-substituted 1*R*,2*R*-DACH, have demonstrated to deeply influence the anticancer activity both *in vitro* and *in vivo*.[2] The DACH analog selected for this work is racemic *trans*-1,2-diamine-4-cyclohexene (DACHEX). The insertion of an unsaturation is sufficient to constrain the structure of the diamine ring in a more rigid half chair conformation. In addition, the unsaturation adds unprecedented π-electrons to the potential nucleophilicity of the six-carbon ring, which in the platinum-DNA adducts is exposed in the major groove. Moreover, the double bond opens the door to a further functionalization of the DACH ligand via electrophilic addition to the carbon-carbon double bond.

Four Pt(II)-DACHEX complexes, differing in the leaving groups (halides or a dicarboxylate) were prepared and assayed for cytotoxicity *in vitro*: *cis*-[$PtCl_2$(DACHEX)], *cis*-[PtI_2(DACHEX)], [Pt(CBDCA)(DACHEX)], and [Pt(OXA)(DACHEX)] (OXA = Oxalate, CBDCA = 1,1-Cyclobutane dicarboxylate).

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Acknowledgements: *we acknowledge the University of Bari (Italy) and the Inter-University Consortium for Research on the Chemistry of Metal Ions in Biological Systems (C.I.R.C.M.S.B.) for support.*

P14 Synthesis and characterization of polymeric nanoparticles for nanomedicine applications

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The field of nanomedicine has attracted more and more interest over the last decades, as nanoparticles (NPs) and polymeric structures have been related to biological and pathophysiological questions. Polymeric NPs were obtained from Poly(methyl methacrylate), P(MMA), Poly(methyl methacrylate-co-acrylic acid), P(MMA-co-AA), and Poly(methyl methacrylate-co-N,N-dimethylacrylamide), P(MMA-co-DMAA) by an emulsion polymerization technique in the presence of Potassium persulfate (KPS) as radical initiator. The reaction conditions were optimized to obtain monodisperse nanoparticles with diameter in the range 50-500 nm and selected samples were loaded with Y^{3+} salt containing a source of Yttrium-89 (^{89}Y) as a model of ^{90}Y [1]. Diethylenetriaminepentaacetic acid (DTPA) was added to MMA/AA copolymers as a chelating agent for Y^{3+}, thus obtaining Yttrium doped polymeric NPs; in the case of P(MMA-co-DMAA) it was not necessary thanks to the presence of functional moieties in the DMAA comonomer. DLS measurements highlight a hydrodynamic diameter in the range 40-180 nm and ζ-Potential $\leq$ -40 mV for P(MMA-co-AA). More polydisperse (DLS range 40-300 nm) and less stable nanoparticles (ζ-Potential $\leq$ -20 mV) were obtained in the case of P(MMA-co-DMAA) based copolymers. FTIR-ATR, UV-vis, XPS and NMR measurements together with AFM and SEM-EDX studies confirmed the structure of the copolymers and evidenced the presence of Y^{3+} on the surface of P(MMA-co-AA). These promising preliminary results will allow us to further extend this study to exploit the preparation of the composite in the presence of Y^{3+} salt containing the ^{90}Y β^- emitting radioisotope, with perspectives in radio-guided surgery (RGS).

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P15 Antimicrobial films of Ethylcellulose and Silver(I) Acylpyrazolonato Complexes for food packaging applications

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In order to extend the shelf-life of aliments and to protect food products, the development of new materials for food packaging is necessary for. Natural biopolymers, including cellulose derivatives have achieved considerable success, due to their high capacity to form films and to their flexibility and transparency. [1] In this work, new antibacterial material for food packaging based on Ethylcellulose and Silver(I) acylpyrazolonato have been developed Silver(I) acylpyrazolonato complexes were synthesized and tested on some bacterial families showing highly toxic effects to microorganisms. [2] Moreover, some Silver(I) complexes can induce van der Waals interaction with the Ethylcellulose matrix because their structural characteristic. To the aim of obtaining Ethylcellulose Silver containing films, two preparation techniques have been used to mix different compositions silver additive/Ethylcellulose ratio: i) through direct dissolution of the reagents in a unique solvent; ii) mixing the powders by Liquid Assisted Grinding, and, then, dissolving the mixture in the suitable solvent. In both cases the resulting solution is allowed to evaporate, obtaining transparent films containing the active silver additives (**Figure 1**). Initially, the solvent used for the preparations was CH_2Cl_2. Subsequently, with the purpose to make the preparation eco-friendly, the 2-Methyltetrahydrofuran has been chosen, due to their environmentally sustainable nature. [3] The antibacterial activity of all films has been tested in agreement to the ISO standard, showing high bactericidal activity. All films have been analyzed with release tests for specific migration of Silver ions, in according to EU Legislation; many of them showing release values lower than EU Legislation limit. [4] Due to their confirmed antimicrobial properties, and to their limited Silver release, according to legislation, films obtained represent highly promising new materials in food packaging industry.

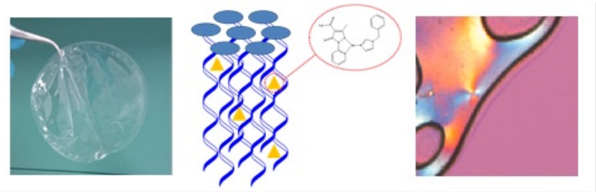

Figure 1: Ethylcellulose Films conteining Silver additives

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[4] EU Food Contact Regulations for Plastics (food packaging and food Regulations 1935/2004, 79/112/EEC and 89/109/EEC) and EU Regulation 10/2011 (The Plastics Regulation), which indicates the rules for measuring overall and specific migration.

P16 Anti-Mackay polyicosahedral clusters in novel *RE-T-M* compounds as hints of metallic glassy behaviour

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The *RE-T-M* compounds (*RE* = rare earth element, Ca, Y; *T* = transition metal; *M* = Mg, Zn, Cd, Al, In) form a huge group, including several *RE*-rich stoichiometries (such as $RE_{23}T_7M_4$ and RE_4TM) which are widely studied with respect both to structural chemistry and physical/chemical properties, such as the glass forming ability.

Yb_9CuMg_4 is the first representative of the so-called "κ-phases" (Hf_9Mo_4B-type, SG: $P6_3/mmc$) formed by a lanthanoid element [1]; after its discovery, a few more isostructural RE_9TMg_4 compounds were reported, with *RE* = heavy rare earth, Y; *T* = Os, Co [2,3].

Recently, two other 9:1:4 compounds with a different *RE* or *T* component were synthesized and structurally characterized by our group, enriching the Hf_9Mo_4B-type family: Y_9NiMg_4 (a=0.9685(2), c=0.9589(5) nm, X-ray powder diffraction) and Ca_9CuMg_4 (a=1.0312(3), c=1.0418(3) nm, X-ray single crystal diffraction).

A structural description unifying the *RE*-rich compounds considered here is based on packing of anti-Mackay polyicosahedral *M*-centered core–shell clusters (PCs, see figure).

On the other hand, these compounds are compositionally close to the line linking the binary phase RE_7T_3 with RE_9TM_4 in the Gibbs triangle. In fact, the structures of phases 4:1:1 (Gd_4RhIn-type), 23:7:4 ($Pr_{23}Ir_7Mg_4$-type) and 15:5:2 ($La_{15}Rh_5Cd_2$-type) can be described as linear intergrowths of the same RE_7T_3 and RE_9TM_4 slabs ("parent types"). Common cristallographic features and the chemical variety make these compounds attractive for the study of crucial criteria governing their formation, useful also for new materials design.

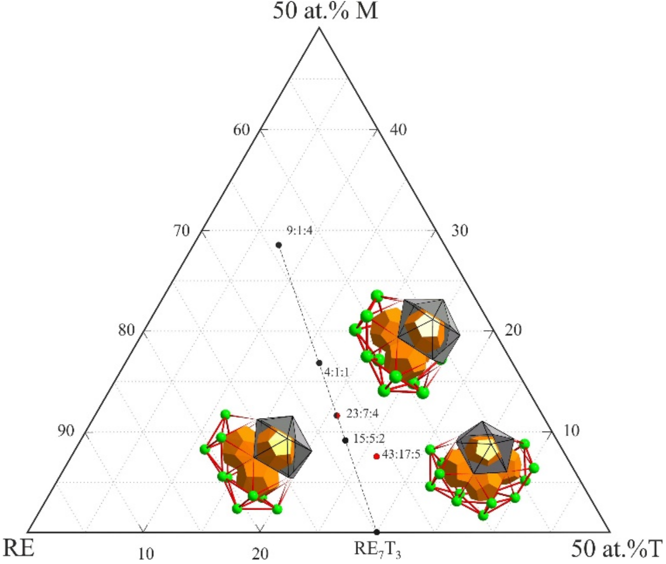

Figure. *RE-rich RE-T-M compounds and their characteristic binary core shell PCs. Phases on the dotted line (black spots) belong to a family of intergrown structures.*

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P17 Experimental thermodynamics, surface and transport properties of liquid Ag-Ge alloys

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The aim of this study is to correlate the thermodynamics of liquid Ag-Ge alloys with their thermophysical properties such as the surface tension, viscosity and electrical resistivity. The Quasi-Chemical Approximation (QCA) for the regular solution and Faber-Ziman theory have been applied to describe the mixing behaviour of Ag-Ge melts in terms of the energetics and structure. The Ag-24.5Ge (at. %) eutectic alloy is worth of investigation because it is widely used as a brazing filler material [1]; in order to determine the melting temperature and the heat of melting of this Ag-Ge eutectic alloy, a Differential Scanning Calorimeter (DSC) has been employed. The DSC instrument was calibrated measuring the melting points and the heat of melting of a known mass of standard materials; after DSC measurements, composition and state of the samples were examined by microscopic analysis (Scanning Electron Microscopy and Electron Probe Microanalysis – SEM/EPMA), see figure 1.

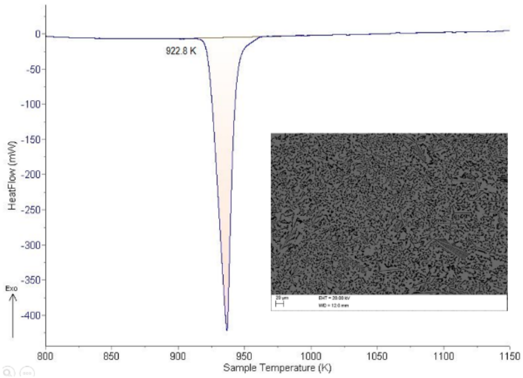

***Figure 1**: DSC cooling curve (5 K/min) and SEM/BSE image of (Ag)+(Ge) eutectic mixture.*

From a technological point of view, particular attention should be paid to the surface tension, a key property of the joining processes. Accordingly, the QCA and Butler's model calculations have been done and subsequently, the model predicted values were compared to available literature data.

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P18 Role of chemical-physical properties in the behaviour of nanomaterials in the gastrointestinal tract.

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Nanomaterials (NM) are extensively used in industry in wide range of applications. As result, the unintentional exposure of humans to these materials could be very common.

Among the various routes of exposure, ingestion is the less studied. Nevertheless, ingestion of NM is very common, since they are used as food additives, and excipient in drugs and cosmetics. There are some evidences that the exposure to NMs can lead to cytotoxic effects to intestinal epithelial cells and can cause alteration of the microbiota [1-2]. Furthermore, the GI tract is a known portal entry of nanomaterials [3].

The biological response to NMs and their fate in the human body largely depends upon the transformation occurring following contact with the biofluids [4]. Due to the complexity of the gastrointestinal tract (GI) the description and prediction of the NM transformation during the journey along the gastrointestinal tract is challenging [5-7].

The aim of this study was to investigate the physico - chemical parameters that influence the fate of nanomaterials after the ingestion, by using a set of NM of different chemical nature and an in vitro system simulating the gastrointestinal tract.

By using a multi-techniques approach we investigate the modification in term of size distribution (DLS, FFF and FPIA) and surface charge (ζ potential). The occurrence of protein corona was also investigated. (DLS, FPIA, ζ potential and the SDS-PAGE). Modification of the surface reactivity leading the production of reactive oxidative species (ROS) was studied after the simulated digestion (EPR – spin trapping).

The results indicate that NM undergo reversible and irreversible changes during digestion, and that such changes are strongly dependents upon the intrinsic properties of the NMs.

The data presented herein contribute to the hazard assessment of NM by defining the biological identity of ingested NMs as well as the driving forces leading transformation along the GI tract.

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Acknowledgements: *This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760928, BIORIMA.*

P19 ^{1}H NMR and elemental profiles of*Xylella fastidiosa* subsp. *pauca*-infected olive trees treated with azinc-copper-citric acid biocomplex

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Xylella fastidiosa subsp. *pauca* is a xylem-limited bacterial phytopathogen associated with the "olive quick decline syndrome" in the Apulia region (Southern Italy). In an attempt to find out possible compounds showing the capacity to reduce the concentration of *X. fastidiosa* within olive leaves, we tested a zinc-copper-citric acid biocomplex on symptomatic sensitive cultivars Ogliarola salentina and Cellina di Nardò olive trees. Through ^{1}H NMR and multivariate statistical analysis, we assessed the metabolomic profiles of extracts from the leaves of the two cultivars, observing an opposite trend concerning the sugars and polyphenols content [1]. Recently, the ^{1}H-NMR-based metabolomic approach was used to provide a snapshot of the plant–pathogen interaction. In both Ogliarola salentina and Cellina di Nardò cultivars, metabolites such as quinic acid, aldehydic form of oleoeuropein, ligstroside and phenolic compounds, were observed as discriminative for the untreated trees in comparison with treated trees. Quinic acid, was confirmed as a disease biomarker for the olive trees infected by *X. fastidiosa*. This study showed how *X. fastidiosa* infection strongly modifies the overall metabolism of olive trees, and how a zinc-copper-citric acid biocomplex could induce an early re-programming of the metabolic pathways in the infected trees [2].

Moreover,in order to deeply analyze the metabolic response to theinfection, inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to characterize the leaf and soil micronutrient content associated with the disease. In particular, we evaluated the magnesium and micronutrients content in soil and leaves samples obtained from infected olive trees. The analysis showed a general lack of molybdenum in soil and uncommon low bioavailability of copper in tree leaves. This could indicate that *X. fastidiosa*infection causes a depletion of copper within olive leaves [3].These results could be useful for the development of strategies for infection containment and plant health promotion.

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P20 Cold plasma pre-treatment improves the germination of wild asparagus seeds

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Wild asparagus (Asparagus acutifoliusL.) is classified in the Liliaceae family that usually grows spontaneously in uncultivated areas. The species could have a high income potential due to its ability to adapt to marginal and arid lands. On the other hand, some limitations exist in the cultivation of this vegetable that contribute to its high cost on the market. The most important is related to its low and erratic seed germination that makes its cultivation economically disadvantageous. Several methods for promoting asparagus seed germination have been proposed in literature: different moist stratification methods (cold, warm, alternate temperature), soaking, hormonal, priming, etc. . In the last decades cold plasma technology is gaining increasing interest in the agriculture scenario. It is a fast, low-cost and pollution-free method to improve seed performance and crop yield by increasing seed germination.

This study evaluates the influence of cold plasma treatment with different gas composition and application times on germination of stratified wild asparagus seed. The effect of cold plasma pretreatment on wild asparagus seeds germination was evaluated. Seed plasma treatments (gas composition: O_2, O_2/N_2, N_2; application times: 1, 15, 30 min) were compared with conventional ones (soaking-H2O, priming-PEG, hormonal-GA3). The importance of seeds stratification and temperature on germination was also investigated

The stratification reduced the time required for germination of about 6 months. Plasma, gas feed with O_2/N_2 for 1 min, resulted more effective in increasing the germination percentage and rate, probably because of increase in water uptake and seed surface decontamination from moulds and fungi.

Wild asparagus is very appreciated by consumers but its selling price is high. The cultivation of this species is a low-input because of its frugality and adaptation to marginal and arid lands. The most important limit of its cultivation is related to low and erratic seed germination. The application of cheap and eco-friendly cold plasma technologies, could help in this aim

P21 Plasma-Deposited Nano-capsules Containing Coatings for Drug Delivery Applications

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A DBD plasma source fed with He, ethylene and an aerosol of a gentamicin solution has been used to deposit the coatings. Discharges were ignited in continuous mode or pulsed mode using a corona power supply. The influence of different deposition parameters has been extensively investigated. SEM analyses were carried out to analyze the morphology of the samples; their chemical composition was investigated by means of XPS, FT-IR and AP-MALDI. The release of gentamicin in water was monitored by means of conductivity meter. The antimicrobial activity and the cytocompatibility of the coatings have been evaluated.

SEM highlighted that, such process, where the drug is supplied in the form of solution aerosol (hence not containing any particles/capsules or alike), leads to a peculiar morphology: a coating with the presence of spherical features whose shape, number, and size depend on the plasma discharge parameters. The hypothesized deposition mechanism involves the polymerization of the monomer fragments directly on the surface of the aerosol droplets in the plasma zone, therefore "freezing" their spherical shape.

FTIR and MALDI-TOF confirm the presence of gentamicin in the coatings.

The agar diffusion assay against P. aeruginosa and S. Aureus confirmed the antibacterial activity of the released gentamicin indicating that the structure modification induced by the plasma concerns only part of the gentamicin load of the coatings and does not compromise the potential of such coatings as drug delivery systems. A preliminary test indicated that gentamicin containing coatings do not cause major concerns to eukaryotic cells (Saos-2 cell line).

P22 Exploring HOPG anion intercalation mechanism through very low-energy Cs ion bombardment

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Highly oriented pyrolytic graphite is usually adopted as a model system to study intercalation mechanisms of solvated ions during electrochemical processes in view of different applications such as fuel cells (energy) or material for graphene production (low-dimension system). To date, the dimensional changes occurring in the electrochemical ion-intercalation process was extensively studied using, e. g., Raman spectroscopy and scanning probe microscopy [1,2]. On the other hand, the chemical aspects related to the intercalation mechanism are still not completely clear.

In this work, we studied the surface and bulk chemistry of HOPG crystals subjected to electrochemical oxidation in sulfuric and perchloric acid solutions. Surface chemistry was investigated through ion/surface collision experiments conducted using a Bi liquid metal ion gun [3]. At the same time, a low-energy caesium ion bombardment was used to exfoliate layer by layer electrochemically treated HOPG samples, thus exploring the surface and layers underneath chemistry.

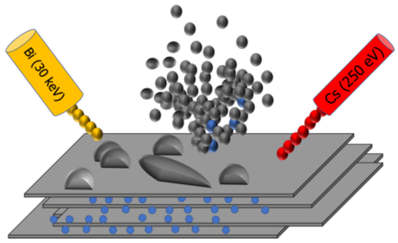

Figure 1: *Scheme of ion/surface collision experiments operated on HOPG after treatment with diluted acid solutions.*

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Acknowledgements: *This research was partially funded by FIRE project.*

P23 Functionalized Noble Metal Nanoparticles as a multifunctional system: from optoelectronics to nanomedicine

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Noble Metal Nanoparticles (MNPs) have been playing important roles in interdisciplinary areas that encompass (bio) chemistry, physics, medicine, materials science and more. Their intrinsic properties are mainly determined by their size, shape, composition, and structural features. One of the main characteristics is their high surface-to-volume ratio and their effects together with the easy access to surface chemistry. A fine tuning of their properties is also allowed by a proper choice of the functionalizing layers, in particular hydrophilic/hydrophobic thiols. In this work, narrow-sized noble MNPs (AuNPs, AgNPs, PdNPs) were synthesized from Au-, Ag-, Pd-salts by a versatile wet chemistry method comprised of sequential reduction, nucleation and growth with mono- and bi-functional, single or mixed thiols as capping agents [1], depicted in fig. 1:

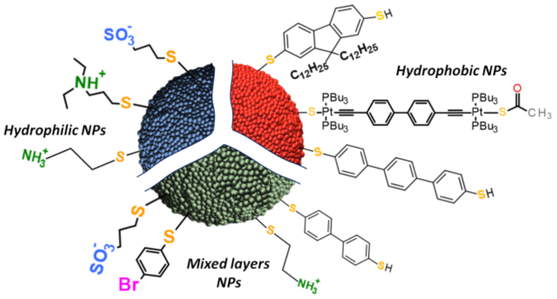

***Figure 1**: Schematic overview of functionalized MNPs*

Surface ligand molecules enable MNPs to disperse in both polar/nonpolar solvents, making them a versatile tool that can be adapted to the aqueous environment as well as to hydrophobic ones. The NMR, UV-vis, DLS, FTIR, XPS, AFM characterizations proved that MNPs are promising multi-functional systems, in which it is possible to combine electrical/photoelectrical LSPR properties with biological activity.

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P24 Luminescent gold(I), silver(I) and copper(I) phosphane complexes with 4-(diphenylphosphanyl)benzoic acid methyl ester as breast cancer growth cells inhibitors.

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Recent findings on the cell growth inhibition effects of phosphane gold(I) complexes, triggered an interest in the research of new gold(I) based entities for cancer chemoterapy drug [1]. Recently it was shown that gold(I) phosphane/azolate complexes were active as anticancer agents for basal like breast cancer. Two selected compounds were chosen for an *in vivo* study in A17 tumors transplanted in syngeneic mice; they resulted to be more active than cisplatin, less nephrotoxic and more tolerated by the mice [2]. However, the presence of a COOH group in only one of the aryl substituents of the phosphane ligand hampers any activity [2]. The methyl esterification of the COOH moiety of the phosphane ligand affords to a new ligand that was employed for the synthesis of three polyphosphane complexes: [tris(4-methylbenzoate)-diphenylphosphanyl)-gold(I)chloride] (1), [tris(4-methylbenzoate)-diphenylphosphanyl)-silver(I)hexafluorophosphate] (2) and [tris(4-methylbenzoate)-diphenylphosphanyl)-copper(I)tetrafluoroborate] (3). The compounds resulted to be stable and strongly luminescent in the solid state. Preliminary MTT tests show that all the compounds were found to be effective, significantly decreasing MDA-MB-231 cells' viability in a dose dependent manner. The MTT tests were performed over 24h and 48h, showing an IC_{50} in the 4-12 µM range.

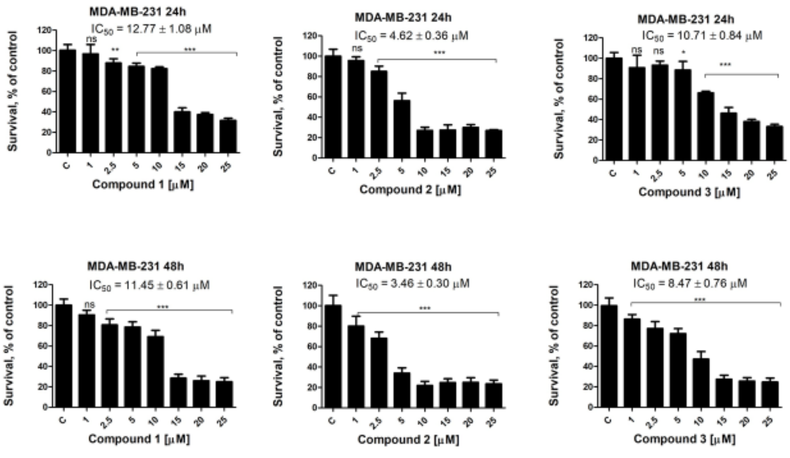

Figure 1: Histograms showing the MTT test results for all the tested compounds for 24 hours (top) and 48 hours (bottom).

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P25 Dispersion of bioactive azolate gold(I) phosphane compounds in lipid lyotropic cubic systems and their structural and biological characterizations.

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Several gold(I) compounds have been found to be active as anticancer agents and among them, some azolate / phosphane gold(I) complexes have been successfully tested against BLB cancer, characterized by strongly severe diagnosis and short life lapse after classic chemotherapy.[1] These findings encouraged us to address our interest towards drug delivery systems able to carry the compounds *in situ* and to preserve their actions. Lyotropic liquid crystalline phases (LCC) were chosen as lipid systems for the encapsulation of these gold compounds.[2] In particular, 3,7,11,15-tetramethylhexadecane-1,2,3-triol (Phyt) and glyceryl monooleate (GMO) were used to encapsulate the tested gold(I) azolate compounds. The physical-chemical modifications due to the presence of the gold compounds within the lipid matrix were studied by SAXS, IR and Raman spectroscopies and by TEM. Figure 1 shows the phase behaviour of Phyt bulk phase upon encapsulation of 3,5-dicyano-imidazolyl-gold(I)-triphenylphosphane. The *in vitro* anticancer activity of GMO/gold compounds nanoparticles was assessed in MDA-MB31 cancer cells and it was found that golds compounds cytotoxicity was maintained upon encapsulation in GMO cubosomes.

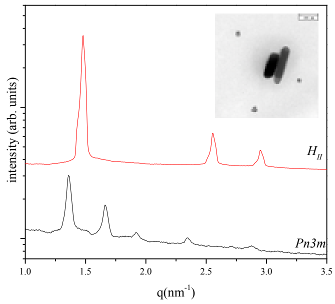

***Figure 1**:* Synchrotron SAXS profiles of PHYT (black line) and PHYT/DM20 (red line) bulk phases. Inset: TEM image of 3,5-dicyano-imidazolyl-gold(I)-triphenylphosphane loaded PHYT hexosomes

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Acknowledgements: *This research was funded by FAR UNICAM and UNIVPM*

P26 Synthesis and spectroscopic characterization of mixed transition metal oxides

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Earth-abundant transition metal and post-transition metal oxides are widely used in semiconductor industry and in catalysis[1,2,3,4] and photo-catalysis[5,6] as well, thanks to their opto-electronic properties. This work explores the reliability and usefulness of new synthetic approach (HEM and Co-precipitation) for mixed metal oxides nano-particles preparation.

Pure oxides with different light absorption properties were used as starting materials. Prepared powder samples were characterized by UV-Visible solid state spectroscopy and their light absorption ability was measured; optical energy band gap was determined by Tauc Plot method[7] and energy band structure was theoretically calculated by a simple approach[8]. Opto-electronic and light absorption properties are found to be directly related to the preparation technique, molar ratio between coupled metals and particles size.

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Acknowledgements: This research was funded by UbiBA and CIRCC.

P27 Free-standing nanofilms by plasma assisted technology

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Technologies based on non equilibrium "cold" plasmas have permeated nowadays several fields, from lights to sterilization, with most processes (etching, deposition of thin films, grafting of chemical groups) focused on surface modification of materials. In the biomedical field, in particular, plasma processes provide surface-activated biomaterials (non fouling surfaces, Tissue Engineering scaffolds with improved cell-colonization, cell-adhesive layers, antibacterial coatings, etc,), sterilization/decontamination methods for materials tissues and wounds and, more recently, newer therapeutic approaches in wound healing and oncology [1]

Freely suspended nanofilms (thickness < 100 nm, NFs) have been a theoretical and experimental curiosity for several decades because, with macroscopic sizes and molecular scale thickness, they combine at the same time the properties of macroscopic materials along with those of individual molecules. We have utiized several plasma deposition processes for depositing NFs characterized by different chemical compositions and properties of biomedical interest, from non fouling to cell-adhesive and antibacterial [2].

In this contribution the plasma deposition of fsNFs of potential applications as biomaterials will be extensively discussed.

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P28 Synthesis of linear and cyclic carbamates from bio-sourced diols and urea

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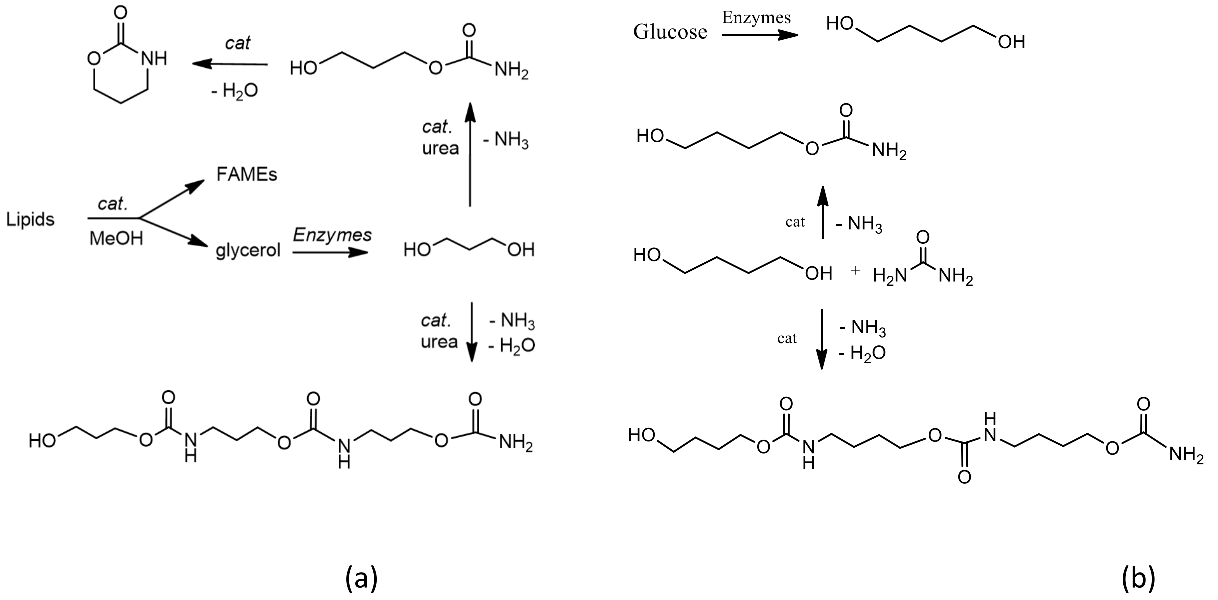
The circular economy model involves zero waste processes that minimize the energy consumption, organic solvents use and reaction by-products. This work is based on the reaction with urea of propane- or butane-diols obtained by the enzymatic conversion of bio-glycerol and glucose, respectively. Target products are cyclic and linear carbamates or directly oligo-urethanes, all high added-value products (Scheme 1a-b). The selectivity of the final product is strongly dependent on the catalyst, reagents molar ratio and reaction conditions used. Noteworthy, urea is industrially produced from ammonia and CO_2. Different cheap catalysts based on oxides of abundant metals on the Earth crust characterized by variable acid/base properties were tested and a variety of reaction conditions were studied.



***Scheme 1a-b**: Linear and cyclic carbamates obtained by reaction of (a) 1,3-propanediol and urea and (b) 1,4-butanediol and urea*

Acknowledgements: This research was funded by UniBa and CIRCC

P29 Dual-action Cisplatin-based Pt(IV) Prodrugs Containing Perillic Acid: Cytotoxic and Antimetastatic Activity.

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Monoterpenes are largely present in the essential oils from citrus and other plants and some of them shown chemopreventive properties [1]. An example is D-limonene, rapidly metabolized by monoxygenases to active oxidized products such as perillic alcohol and perillic acid (PA). PA inhibits the proliferation of A549 lung cancer cells and, importantly, sensitizes them to the cytotoxic action of cisplatin. An efficient co-administration of cisplatin and PA can be achieved using the corresponding Pt(IV) "combo" complexes. Pt(IV) conjugates are considered prodrugs since they can be reduced in the hypoxic (and then reducing) intracellular milieu of tumor cells to cytotoxic cisplatin with the loss of their two axial ligands (*i.e.*, the auxiliary drug; *activation by reduction*) [2].

The cisplatin-based *cis,cis,trans*-[$Pt^{(IV)}(NH_3)_2(Cl)_2(Ac)(PA)$], **1**, and *cis,cis,trans*-[$Pt^{(IV)}(NH_3)_2(Cl)_2(PA)_2$], **2** (Ac = acetato; Figure 1), shows antiproliferative and cytotoxic activity (as verified by the activation of caspase 3/7) in the low nanomolar range for the latter. Interestingly enough, **1** and **2** exhibit antimetastatic activity as proved by means of cell migration and invasion assays (wound healing and Matrigel assay) [3]. Thus **1** and **2** are promising dual-action "combo" Pt(IV) conjugates worthy of further preclinical development.

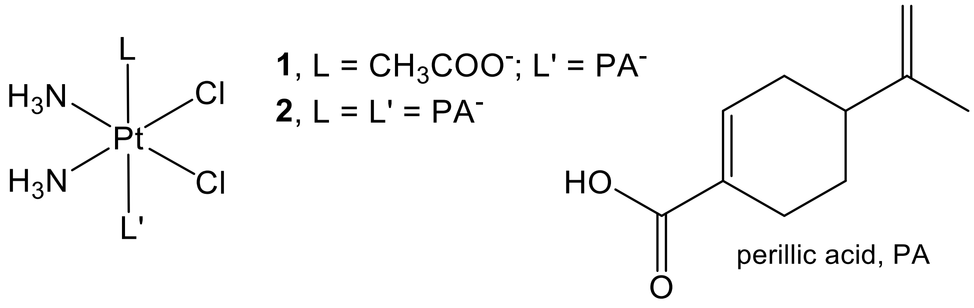

Figure 1*: Sketch of the cis,cis,trans-[$Pt^{(IV)}(NH_3)_2(Cl)_2(Ac)(PA)$],* ***1****, and cis,cis,trans-[$Pt^{(IV)}(NH_3)_2(Cl)_2(PA)_2$],* **2***, complexes.*

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P30 Profiling proteasome activity by porphyrins

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Porphyrins (from the Greek for "purple") are very special molecules. They are ubiquitous, naturally occurring, and are involved in a wide variety of important biological processes ranging from oxygen transport to the regulation of many biochemical pathways. Learning from Nature, chemists have been using these ring-shaped molecules for a vast assortment of purposes. In particular, the possibility to tailor their physical and chemical properties at the molecular level, make porphyrins extremely versatile and attractive synthetic base materials for the design of cutting-edge theranostic probes. In oncology, porphyrins find extended application as photosensitizers in photodynamic therapy (PDT), boron carriers in boron neutron capture therapy (BNCT) and telomerase inhibitors.

Inspired by their attractive properties we have been investigating the ability of porphyrins to inhibit proteasome activity in vitro and in cell-free systems. Cationic porphyrins - depending on the spatial distribution of their electrostatic charges – exhibit an amazing variety of binding modes and inhibition mechanisms. First, they may bind to the 20S proteasome gates causing their partial occlusion by competitively hindering the entrance of the substrate into the catalytic chamber. Second, they may fly over different α subunits thus affecting the dynamic equilibrium between the open and the closed state of the proteasome gates. Additional binding modes, all resulting in allosteric inhibition mechanisms, involve interactions with the grooves connecting α- and β-rings as well as with the β5 catalytic subunits on their own. This evidence convinced us that charged substituents represent a sort of key code able to fine-tune the ability of porphyrins to interfere with proteasome gating phenomena. We also observed that, if added to the latent 20 S proteasome, anionic porphyrins may even activate the core particle by facilitating the access of the substrate to the proteasome interior.

Taken as a whole, our studies suggest that porphryins represent a unique class of proteasome binding molecules endowed with either inhibiting or activating potencies. Based also on the evidence that allosteric proteasome regulation is becoming increasingly important in the treatment of many diseases including cancer and neurodegeneration, we hope that our results may pave the way to studies aimed at designing ever more sophisticated proteasome modulators.

Acknowledgements: *This research was funded by Miur-Prin 2015*

P31 Cerium containing mesoporous glasses/alginate hybrid materials for the controlled release of curcumin: from *in vitro* to *in vivo*.

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Hybrid biomaterials find important uses in many fields since they synergize the beneficial properties of different materials and substances into a superior matrix. Particularly interesting are biomedical applications in which they can be exploited for tissue regeneration and as drug delivery systems. In literature there are many examples of biomaterials capable of releasing molecules, ions or nanoparticles that act as antioxidants [1]. In this study we report the development of a stable hybrid material that combines the enzyme-like activities (Catalase and SOD) [2] of a Bioglass based on Hench´s 45S5 Bioglass® modified by Ce^{4+}/Ce^{3+} ions and the antioxidant properties of curcumin. In order to preserve antioxidant properties and to enhance biocompatibility and uptake, calcium alginate hydrogels were used to formulate the new hybrid material.

In this study, a mesoporous bioactive glass ($80SiO_2$–$15CaO$–$5P_2O_5$ mol-%) with 5.3 mol-% of CeO_2 (Ce-MBG) was synthetized and used together with curcumin to produce micro-beads by ionic cross-linking of alginate. The samples were tested *in vitro* for their biological properties and pharmacokinetics profiles in physiological media (simulated gastric fluid and simulated intestinal fluid). Finally, their uptake and distribution was tested *in vivo* on a Wistar rat animal model, suggesting potential applications for the development of new therapeutics.

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P32 Investigation of glycoside derivative as ligand for biomedically relevant lectins: molecular modeling and binding analysis

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Galectins are carbohydrate-binding proteins able to recognise β-galactoside sugars with high specificity. They have important functions in several aspects of cancer biology, such as in regulation of apoptosis, tumour metastasis, migration, and angiogenesis[1]. Therefore, development of potent and selective inhibitors capable of reducing the activity of galectins is of great importance. Many natural or synthetic carbohydrate ligands of galectins can inhibit their biological activity, even to nanomolar range[2]. Simple molecules containing two saccharide residues with a bridging sulfur atom can display high affinity towards galectins and potential anti-cancer activity[3]. In this context, we design and synthetized a diglycosylated compound equipped with alternative bridging group between the sugars such as a selenium moiety, an essential trace element exhibiting cytotoxic properties, to obtain a new candidate for mimicking carbohydrate ligand galectins. To this aim, binding affinity analysis of digalactosyl selenide was performed in comparison with its counterpart containing a sulphur. All the results will be widely discussed proposing the digalactosyl selenide as a starting compound for the design of novel appealing molecules acting as therapeutic agents via galectin dependent mechanism.

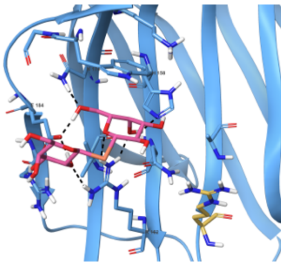

***Figure**: Galectin 3 (cyan) in complex with the digalactosyl selenide (magenta). Important residues for the binding are depicted in (cyan) sticks.*

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P33 Gadolinium-loaded hard-shelled glycolchitosan nanodroplets/bubbles as dual MRI/Ultrasound detection of drug delivery and release: a proof of concept study

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The purpose of this work was to develop a bimodal US/MRI theranostic system where echography may give information about drug delivery, and MRI may provide an imaging response dependent on the drug release.

The core-shell system was composed by a coating of glycol-chitosan cross-linked with sodium triphosphate and a core filled by perfluoropentane, which is liquid at RT and gas at physiological temperature. The nanocarrier was loaded with the steroid-like anti-inflammatory/antitumor pro-drug prednisolone phosphate (PLP) and the PLP-mimicking MRI contrast agent Gd-DTPAMA-CHOL (Fig. 1). The nanodroplets displayed a hydrodynamic diameter in the range 540-560 nm (PDI 0.1) and Z-potential values between 13 mV and 18 mV. Monitoring the morphology by optical microscopy showed a good stability and no changes in size/morphology were observed up to 3 months. Upon heating above 29°C, nanodroplets became nanobubbles with a consequent size increase. The system was stable in serum where induced a haemolytic activity < 1 %. Release measurements *in vitro* indicated that PLP and Gd-DTPAMA-CHOL shared a similar kinetic profile with a release at 12 h lower than 4 %. The ability of Gd-DTPAMA-CHOL to generate MRI contrast was extremely sensitive to its location: the relaxivity of the agent loaded to the particles is almost 600 % higher than the released free agent. Taken collectively, the results obtained demonstrate the good potential of hard-shelled glycol-chitosan particles loaded with a drug and a drug-mimicking MRI agent for a dual US/MRI detection of drug delivery and drug release.

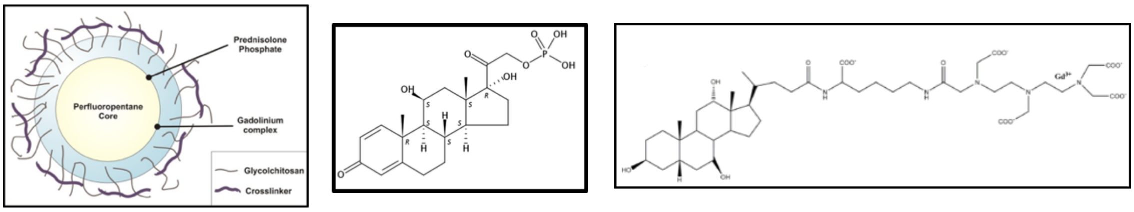

***Figure 1**: Left: schematic representation of the nanodroplets/bubbles loaded with the drug PLP (middle), and a paramagnetic Gd(III) complex (right)*

P34 Aerosol-assisted atmospheric pressure plasma deposition of photocatalytic thin films for the degradation of organic pollulants

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Over the last years, aerosol-assisted atmospheric pressure cold plasma processes have attracted growing interest in thin film deposition, since they allow, for instance, the easy preparation of nanocomposite (NC) coatings consisting of inorganic nanoparticles (NPs) and an organic or inorganic matrix [1,2].

In this work an atmospheric pressure dielectric barrier discharge fed with helium and the aerosol of a dispersion of photocatalytic NPs (i.e., oleate-capped TiO_2 P25) in liquid hydrocarbon precursors (i.e., octane/1,7-octadiene mixture) has been used to deposit organic-inorganic NC coatings. The deposition process has been optimized on both flat and three-dimensional macroporous supports (i.e., glass slides and open-cell polyurethane foams with pore density of 45 ppi, respectively), allowing the preparation of novel materials with photocatalytic properties. The chemical composition of the deposited films, investigated by Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), combines the typical features of the NPs and the hydrocarbon polymer deriving from the plasma polymerization of the precursors. Moreover, as confirmed by scanning electron spectroscopy (SEM) images, the coatings consist of quasi-spherical NPs agglomerates covered by the polymer.

The photocatalytic properties of coatings have been studied by evaluating their ability to degrade an organic target molecule (methyl orange, MO) in aqueous solution, under UV irradiation. To achieve this goal a small recirculating reactor operating in batch mode with a photocatalytic cell connected to a peristaltic pump and an optical detector has been purposely designed. Degradation kinetics have been obtained for both flat and 3D porous samples by monitoring the MO UV-vis absorption spectra during the irradiation time. Preliminary results are promising and suggest the possible utilization of these materials in wastewater treatment due to the simple recovery after photocatalytic reaction and the efficient recyclability.

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P35 Terpyridine functionalized cyclodextrin nanoparticles: metal coordination for targeted drug delivery?

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Cyclodextrin (CD) nanoparticles have been chemically modifed introducing new properties available for their application in the biological systems, such as targeting units [1] or chelating units [2]. Supramolecular host–guest chemistry has been used to add recognition motif on CD-based nanoparticles (NPs).
We exploited the coordination ability of terpyridine and functionalized NPs based on CD polymers with terpiridine moieties.
Here we report the synthesis of CD-based NPs contaning terpyridine units (pCDtpy) and their metal complexes (Fig. 1). The presence of CDs confers water solubility to the systems and improve the application of terpyridine chemistry. Furthermore, we synthesized ternary complexes with the polymer, iron(II) and a biotin derivative of terpyridine. We choose biotin as the targeting unit because it is a cellular growth promoter and its content in tumors is higher than in normal tissues [3]·
Preliminary results show that the doxorubicin cytotoxicity was not reduced in the presence of pCDtpy and of its iron complex with the biotine conjugate, and was slightly improved in the presence of pCDtpy and copper(II).

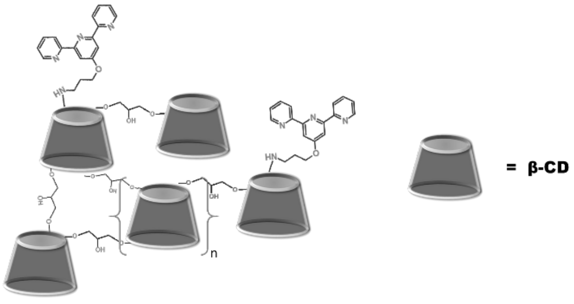

***Figure 1**: Schematic structure of pCDtpy*

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P36 Homo/Heterobimetallic Trinuclear Coinage Metals's Metallacycles.

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Homonuclear Coinage metals Trinuclear metallaCycles (CTC) are a class of C, N or N,N coordination compounds that are known since 1970's.[1] Their synthesis proceeds by the proton abstraction from the azolate and subsequent metalation with proper metal sources or rearrangement of nitriles to carbeniate in basic environment. The homonuclear compounds exhibit sophisticated emissive, molecular recognition, metalloaromaticity properties, but the interest on these compounds was recently renewed because the unprecedented optoelectronic properties such as near unit quantum yield,[2] VOC adsorption[3] and their application in OLED found for heterobimetallic Au/Cu CTC compounds. By mixing solutions of homonuclear CTC with different metals and different ligands, heterobimetallic CTCs are obtained as well as π-π stacking supramolecular structures.[2] Heterobimetallic Ag/Au and Cu/Au compounds are strongly luminescent showing both fluorescence and phosphorescence phenomena both in the solid and solution states (Figure 1).

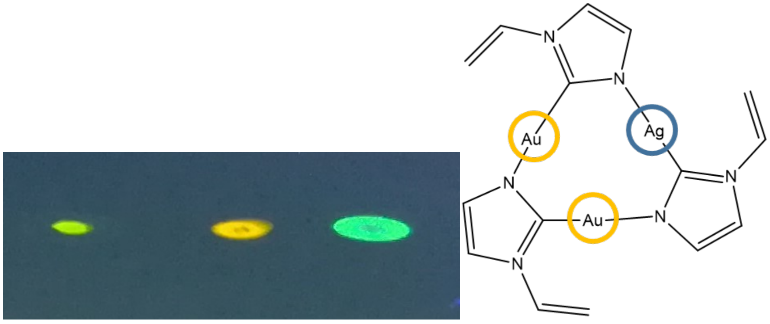

***Figure X**: Luminescence of trinuclear metallacycles on a TLC upon excitation at 366 nm (mixed metal mixed ligand, Au2Ag left spot, mixed metal Au2Ag central spot, TRBzimAu right spot).Schematic view of a mixed metal Au2Ag CTC.*

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P37 Cytotoxicity of a Novel Class of Organo-Diiron Complexes

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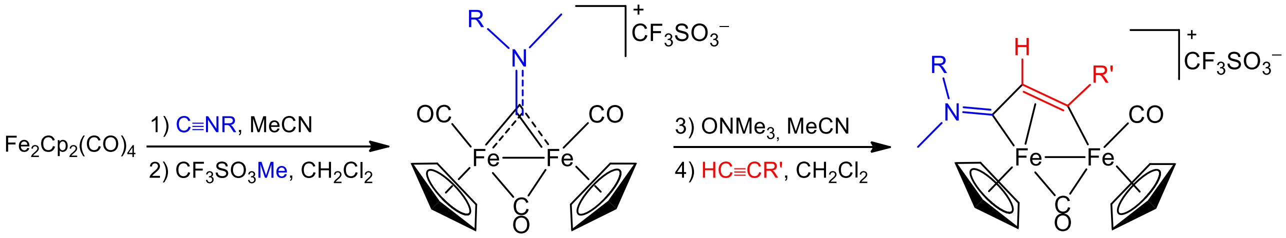
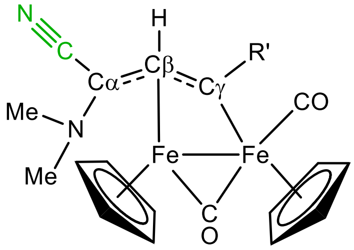
Organometallic diiron complexes containing a bridging vinyliminium ligand can be synthesised using a gram-scale procedure, starting from the commercially available $Fe_2Cp_2(CO)_4$, *via* stepwise assembly of isocyanide, methyl and alkyne moieties. The synthetic pathway (see scheme below) has a general validity and has been used to prepare a wide variety of complexes with different R and R' substituents and, consequently, different physical-chemical properties.



The cationic vinyliminium complexes can undergo nucleophilic attack, which is facilitated by their net positive charge. Thus, diiron cyano-amino-allylidene complexes (see figure below) can be prepared *via* regio-selective addition of cyanide (from NBu_4CN) to the C_α carbon of the bridging C_3-ligand. This is a feasible strategy to accomplish clean and facile C-C bond formation.



Despite being classical organometallic complexes, all products are air/water stable and the parent vinyliminium compounds also display satisfying water solubility (up to 9 g/L). The cytotoxic activity towards A2780 and A2780-cisR cancer cell lines and non-tumorigenic ovarian HEK-293 cells has been determined for selected compounds. The IC_{50} values indicate that the antiproliferative activity and the selectivity towards cancer cells can be tuned by a proper modification of R and R' substituents.

In order to shed more light on the mechanism of action, electrochemical analysis, ROS production assessment and interaction studies with model biomolecules have been carried out.

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P38 Mono- and Pentanuclear Al^{III} and Ga^{III} Complexes of Tetrakis-2,3-[5,6-di(2'-pyridyl)pyrazino]porphyrazine: Synthesis, Physicochemical Properties and Photoactivity in Photodynamic Therapy

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Ida Pettiti,[a] Karl, M. Kadish[b]

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In our previous studies we devoted our attention to the synthesis and characterization of new porphyrazine macrocycles having heterocyclic rings *o*-condensed on the external sites of the pyrrole groups [1]. Among them, deeply studied were the tetrakis(thiadiazole)porphyrazine complexes [TTDPzM] (M = Mg^{II}(H$_2$O), Zn^{II}) and [TTDPzMCl] (M = Al^{III}, Ga^{III}) (Figure 1A), the structure of which was elucidated by single crystal X-ray work [2]. Photoactivity for the generation of singlet oxygen, $^1O_2$, the key cytotoxic agent in photodynamic therapy (PDT) [3], was also previously monitored for these compounds in DMF or DMF/HCl solutions with obtained quantum yield values (Φ_Δ) in DMF/HCl increasing for the series in the order: Mg^{II} (0.30) < Al^{III} (0.35) < Zn^{II} (0.52) < Ga^{III} (0.69) [4]. These results suggested to explore the photoactivity of the new series of Al^{III} and Ga^{III} complexes of formula [Py$_8$TPyzPzMX]·xH$_2$O (M = Al^{III}, Ga^{III}; X = Cl$^-$, OH$^-$), shown in Figure 1B, and their related pentanuclear derivatives [(PdCl$_2$)$_4$Py$_8$TPyzPzMCl]·xH$_2$O (M = Al^{III}, Ga^{III}) carrying externally coordinated PdCl$_2$ units. Of these new macrocycles details are given on the synthetic procedures and their general physicochemical and electrochemical properties. The ability of these compounds to generate singlet oxygen for applications in PDT is also reported and discussed.

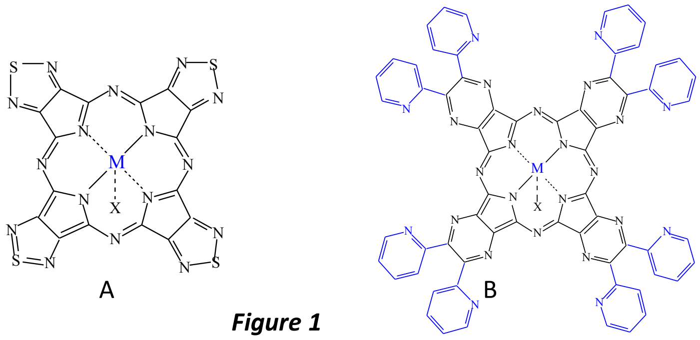

Figure 1

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P39 Metal Ion Binding Ability of the N-terminal region of Tau Protein: the use of model peptides for the evaluation of metal ion binding preferences.

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Tau protein belongs to a family of microtubule-associated proteins (MAPs) specifically expressed in neurons.[1] Tau hyper-phosphorylation triggers toxic deposition of this protein, that in turn causes the formation of intracellular Tau paired helical filaments (PHF), which ultimately gather together to form the characteristic neurofibrillary tangles (NFT).[2,3] The formation of intracellular neurofibrillary tangles (NFT) and the accumulation of amyloid-beta (Aβ) within extracellular senile plaques, represent the most common clinical hallmarks in the brain of AD patients.[4,5] There is evidence that some transition metals such as copper, zinc and iron might be implicated in the neurodegenerative process of the disease.[6]

The role of transition metal ions in modulating Aβ's aggregation, fibrillogenesis and toxicity has exhaustively been reported.[7] By contrast, the association of metals with Tau protein has only recently become relevant to the pathogenesis of AD[8] even if their role in tauopathies is controversial.[9,10]

Several biophysical and structural studies have revealed binding of Cu2+ ions with full-length Tau protein[11] as well as short peptide comprising the first, second or third repeat of Tau microtubule domain.[12] Although increased levels of peptide fragments from the N-terminal portion of Tau protein have been detected in the cerebrospinal fluid (CSF) of AD patients,[13] only few work has been reported about the metal complexes with peptides derived from this region.[14] In particular, the Cu^{2+}-binding features of two peptide fragments, encompassing the 1–25 or 26–44 residues of the human Tau protein sequence were investigated. The overall results indicated that copper(II) can bind these peptides using the histidine residues 14 and 32, or the N-terminal amino group as anchoring sites.

In the present study we described the molecular features of copper(II) complexes of different peptides fragments belonging to N-terminal regions of Tau protein. The peptides synthetized in this work include the terminally blocked sequences of Tau(9-16) and Tau(26-33). The stability constants, together with complex speciation and stoichiometry of the copper(II) complexes, were determined by means of potentiometric titrations and ESI-MS spectrometry respectively. In addition, the EPR and far-UV CD studies were helpful to infer the coordination environment and the metal ion induced conformational changes within the peptide chain. Finally, in order to get complementary information about the key residues involved in the copper(II) coordination, we carried out a series of the tandem mass spectrometry measurements. Interestingly, the study of the copper(II) complex species with the Tau(9-16) fragment revealed the formation of mononuclear and dinuclear complexes while only mononuclear species were observed in the case of the copper(II)-Tau(26-33) system.

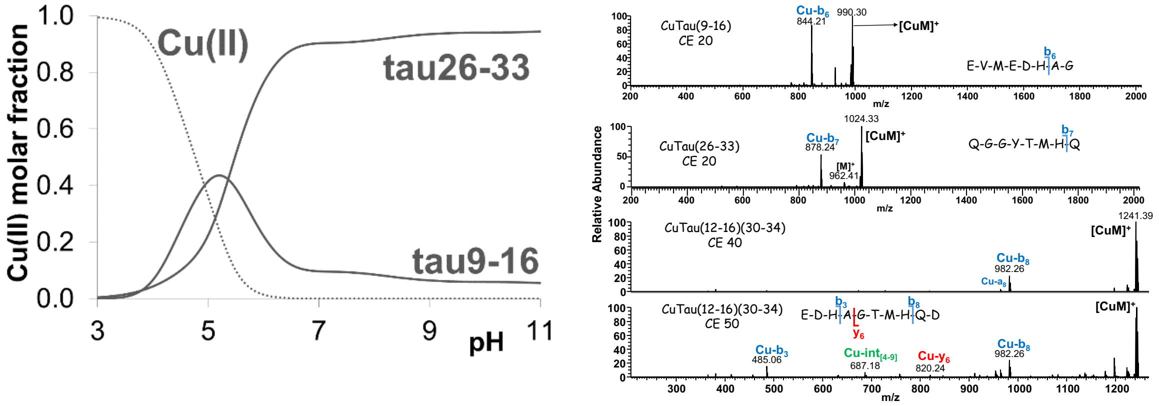

***Figure 1**: Concentration distribution of Cu(II) ion between the peptide model systems. HCD spectra of single charged copper complexes with the studied peptides at CE 40 and CE 50.*

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P40 Chemical Recycling of poly(bisphenol A carbonate) *via* Hydrolytic Cleavage of Ester Bond under Rare Earth Metal Triflates Catalysis

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Lewis acids $M(O_3SCF_3)_3$ (M = Sc, Yb, La) triflate salts have been used as catalysts of the hydrolysis reaction of poly-(bisphenol A carbonate) (PC), which is an attractive route to the chemical recycling and valorization of waste PC.[1] In THF, the $M(O_3SCF_3)_3$ salts effectively catalyzed the hydrolysis of PC to bisphenol A (BPA) and CO_2. $La(O_3SCF_3)_3$ promoted the depolymerization of the polymer with the highest BPA yield and selectively, as, unlike the other triflates investigated, it displayed also very poor tendency to promote, under the working conditions, the decomposition of the monomer (BPA) to phenol, 4-isopropenylphenol and 4-isopropylphenol. The influence of a few experimental parameters on the catalytic activity of $La(O_3SCF_3)_3$ has been investigated. An excessive amount of H_2O in the reaction mixture lowers the productivity of the process. Using a H_2O/PC weight ratio close to unity the depolymerization can proceed with high yield (~97% after 6 h) under not severe temperature conditions (433 K) in the presence of moderate catalyst loads (10 mol%). Rising temperature increases the conversion rate of PC but also causes the diminution of BPA selectivity, which, however, can be kept in modest limits by suitably controlling the reaction time. The $La(O_3SCF_3)_3$ catalyst can be recovered quantitatively at the end of the reaction and reused. The catalytic behavior of the $M(O_3SCF_3)_3$ salts has been compared with that of a strong proton donor such as CF_3SO_3H. The results obtained allow to exclude that protons arising from $[L_nM(OH_2)]^{3+}$ (L = ligand (H_2O, THF, etc)) aquo-complexes might play a catalytically important role in promoting the depolymerization process.

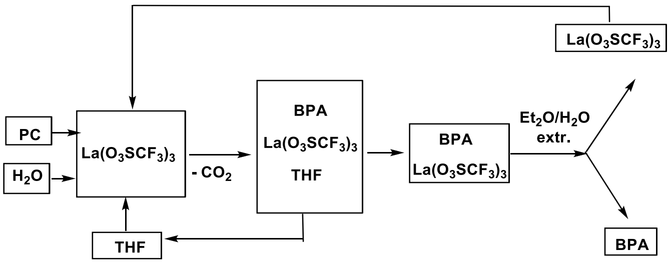

***Figure 1**: Hydrolysis of poly-(bisphenol A carbonate) promoted by $M(O_3SCF_3)_3$*

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P41 Unravelling the effect of ZrO_2 modifiers on the nature of active sites on $AuRu/ZrO_2$ catalysts for furfural hydrogenation

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Furfural is traditionally produced from renewable lignocellulosic biomass and it is an ideal feedstock for the sustainable production of value-added chemicals and biofuels [1]. Furfural catalytic hydrogenation yields a variety of products, such as furfuryl alcohol, 2-methylfuran and tetrahydrofurfuryl alcohol [2]. The hydrogenation of furfural has been studied using mono- or bimetallic noble-metal catalysts mostly consisting of Pd, and Ru [3-4]. To tailor the selectivity to the desired product, it is important to tune the metal structure, but also the acid-base properties of the support. In this work, Ru and AuRu nanoparticles were prepared by sol-immobilization methodology and deposited on different functionalized ZrO_2 (ZrO_2, Y-ZrO_2 and La-ZrO_2). The catalysts were characterized by analytic transmission electron microscopy (TEM) and Fourier Transform Infrared Spectroscopy (FTIR). TEM and FTIR confirmed the bimetallic nature of AuRu particles with an average size of 4-5 nm. The catalysts were tested in the furfural hydrogenation using isopropanol as hydrogen donor. The addition of Au to Ru did not significantly modify the activity and selectivity, but enhanced the resistance to deactivation. Moreover, the acid-base properties were monitored by acetonitrile adsorption followed by FTIR spectroscopy. It was shown that the acidity of the support greatly influences the selectivity. In particular, 71% selectivity to gamma-valerolactone was achieved over AuRu/Y-ZrO_2,due to the modified acidic strength of Zr^{4+} sites on the Y-doped oxide.

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P42 Modulating the water oxidation catalytic activity of dimeric iridium complexes by functionalizing the Cp*-ancillary ligand

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Over the last decade, organoiridium complexes have been successfully exploited as precursors of water oxidation catalysts (WOCs).[1] Most of them can be formulated as $[Cp^*IrL_1L_2X]^n$ where L_1 and L_2 might be two monodentate or a bidentate ligand(s), whereas X is H_2O or a labile ligand easily exchangeable with H_2O.[2] Despite many studies have been performed to understand how the nature of L_1 and L_2 affect the performances of such Ir WOCs, to the best of our knowledge, no attention has been dedicated to functionalize the Cp* ancillary ligand.

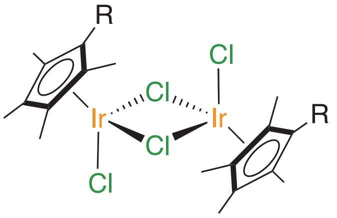

***Figure 1**: Sketch of the investigated Ir-dimers*

For this reason, we decided to evaluate how the catalytic activity of $[^{R}Cp^*IrCl(\mu\text{-}Cl)]_2$ (R = H, Me, Et, Pr, Ph, Bz, 4F-Ph, 4OH-Ph, and $CH_2CH_2NH_2$) dimeric precursors toward $NaIO_4$ driven WO, at 298 K and pH = 7 (by phosphate buffer), depends on the nature of R. For each dimer, the effect of changing catalyst (1-10 μM) and $NaIO_4$ (5-40 mM) concentration has been studied. All precursors exhibit a high activity with TOF values ranging from 130 min^{-1} to 350 min^{-1} and TON values being always those expected assuming a 100% yield. The catalytic activity was strongly affected by the nature of the R substituent. Highest TOF values were observed when R was little encumbered and electron-donating.

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