

XLIII Congresso Nazionale di Chimica Inorganica

Inorg2015

Camerino 9 - 12 settembre 2015

Atti del Congresso



XLIII Congresso Nazionale della Divisione di Chimica Inorganica della Società Chimica Italiana
Camerino 9-12 settembre 2015



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9 SEPT <i>Teatro Filippo Marchetti</i>		10 SEPT <i>Sala della Muta, Palazzo Ducale</i>		11 SEPT <i>Sala della Muta, Palazzo Ducale</i>		12 SEPT <i>Sala della Muta, Palazzo Ducale</i>	
08:00	REGISTRATION <i>(Sala della Muta)</i>	9:00	PL3 BONATI LECTURE PAUL DYSON	09:00	PL4 CHINI LECTURE ANTONIO TOGNI	09:00	PL5 UNICAM CHEMISTRY LECTURE OMAR YAGHI
10:00	OPENING CEREMONY			10:00	CREDI (OR11) STAGNI (OR12) TAGLIATESTA (OR 13) GRAIFF (OR14)	10:00	BENEDETTI (OR19) CHIAVARINO (OR20) CASELLI (OR21) PELAGATTI (OR22)
10:30	PL1 SACCONI MEDAL TOBIN MARKS	11:00	Coffee break	11:00	Coffee break	11:00	Coffee break
11:30	Coffee break	11:30	KN3 PIERLUIGI BARBARO	11:30	KN6 ANTONINO MARTORANA	11:30	KN8 ROSSANA GALASSI
12:00	KN 1 PhD PRIZE MATTEO ATZORI	12:00	CRESTONI (OR15) CALVILLO (OR16) CIABATTI (OR17) PLASTINA (OR18)	12:00	TONUCCI (OR23) GIAMELLO (OR24) MARRANI (OR25) PICA (OR26)	12:00	NOSCHESE (OR31) VILLA (OR32) VENDITTI (OR 33) DONNADIO (OR34)
12:30	BARATTA (OR1) BUCCI (OR2)	13:00	Lunch break	13:00	Lunch break	13:00	CLOSING CEREMONY
13:00	Welcome Lunch						
9 SEPT <i>Sala della Muta, Palazzo Ducale</i>		14:30	Sessione Poster Coffe break	14:30	Sessione Poster Coffe break		
15:00	PL 2 NASINI MEDAL STEFANO AGNOLI						
16:00	CESARI (OR3) MONTICELLI (OR4) MARCHETTI (OR5) RANCAN (OR6)	17:00	KN4 SILVIA GROSS	16:30	KN7 LAURA PRATI		
17:00	Coffee break	17:30	KN5 ANTONELLA ACCARDO	17:00	SOCIAL TOUR		
17:30	KN2 CARLO NERVI	18:00	Divisional Assembly				
18:00	MILANI (OR7) GALLO (OR8) BIFFIS (OR9) ZACCARO (OR10)						
19:00	GICO Committee Meeting		Plenary and Key-notes dinner	20:30	Social Dinner		

Programma scientifico

Mercoledì 9 settembre (*Teatro Filippo Marchetti*)

10:00	Apertura del Congresso Saluti delle autorità accademiche e cittadine Saluto del Presidente della Divisione (Adriana Saccone)	
	Chair: Maurizio Peruzzini	
10:30	PL1	Medaglia Luigi Sacconi <u>Tobin Marks</u> , Northwestern University, USA <i>Interface Science of Soft Matter Photovoltaics</i>
12:15	Coffee break	
	Chair: Emma Gallo	
12:30	KN1	Premio per la miglior tesi di Dottorato in Chimica Inorganica <u>M. Atzori</u> , F. Artizzu, A. Serpe, P. Deplano, P. Auban-Senzier, E. Canadell, F. Pop, N. Avarvari, M. L. Mercuri <i>Anilate-based Functional Molecular Materials with Conducting and Magnetic Properties</i>
13:00	OC1	<u>W. Baratta</u> , S. Baldino, S. Giboulot, S. Facchetti, H. G. Nedden, A. Zanotti-Gerosa <i>Pincer 4-Functionalized 2-Aminomethylbenzo[h]quinoline Ruthenium Catalysts for Aldehyde / Ketone Reduction</i>
13:15	OC2	<u>Alberto Bucci</u> , Gabriel Menendez Rodriguez, Gianfranco Bellachioma, Cristiano Zuccaccia, Alceo Macchioni <i>Positional Effect of a Hydroxyl Group on the Activity of Pyridyl-Carboxylate and -Aminidate Cp*Ir-Catalysts for Water Oxidation</i>
13:30	Buffet di benvenuto	

Mercoledì 9 settembre (*Sala della Muta, Palazzo Ducale*)

	Chair: Adriana Saccone	
15:00	PL2	Premio Raffaele Nasini <u>Stefano Agnoli</u> , Università di Padova, Italy. <i>Interfaces at the nanoscale: a new paradigm in catalysis</i>
16:00	OC3	<u>Cristiana Cesari</u> , Andrea Cingolani, Rita Mazzoni, Chiara Parise, Stefano Zacchini, Valerio Zanotti <i>Synthesis of novel Ru N-Heterocyclic carbene complexes for bifunctional metal-ligand catalysis</i>
16:15	OC4	<u>Marco Monticelli</u> , Cristina Tubaro, Claudia Graiff, Gianluca Accorsi <i>Metal complexes with di(N-heterocyclic carbene) ligands bearing an ortho-, meta or para-phenylene bridge</i>
16:30	OC5	<u>Fabio Marchetti</u> , Marco Bortoluzzi, Eleonora Ferretti, Guido Pampaloni, Stefano Zacchini <i>NHC Complexes of High Valent Niobium and Tantalum Halides</i>

16:45	OC6	<u>Marzio Rancan</u> , Jacopo Tessarolo, Silvio Quici, Lidia Armelao <i>A coordination-driven pocket as nanoreactor and nanovessel</i>
Chair: Alceo Macchioni		
17:30	KN2	<u>Carlo Nervi</u> , Roberto Gobetto <i>Transition Metal Complex Catalysts for the Electrochemical Reduction of CO₂</i>
18:00	OC7	<u>Barbara Milani</u> , Vera Rosar, Tiziano Montini, Gabriele Balducci, Paolo Fornasiero <i>From nonsymmetric BIANs to nonsymmetric DABs: towards efficient Pd-catalysts for functionalized polyolefin synthesis</i>
18:15	OC8	<u>Emma Gallo</u> , Paolo Zardi, Daniela Maria Carminati, Daniela Intriari <i>Synthesis of Biological Aminated Compounds Catalysed by Ruthenium Porphyrin Complexes</i>
18:30	OC9	<u>Andrea Biffis</u> , Cristina Tubaro, Anatoliy P. Marchenko, Georgiy N. Koidan, Anastasiya N. Hurieva, Yuri Vlasenko, Aleksandr N. Kostyuk <i>Palladium complexes with chelating N-Phosphanyl-Carbene Ligands: Synthesis and Catalysis</i>
18:45	OC10	G. Valente, N. Depalo, I. de Paola, R. M. Iacobazzi, N. Denora, V. Laquintana, R. Comparelli, E. Altamura, T. Latronico, M. Altomare, E. Fanizza, M. Striccoli, A. Agostiano, M. Saviano, A. Del Gatto, and M. L. Curri and <u>L. Zaccaro</u> <i>Integrin Targeting with Peptide Bioconjugated Nanocrystalline Heterostructures: a Theranostic Prospect</i>
19:00	Riunione Consiglio GICO	

Giovedì 10 settembre (Sala della Muta, Palazzo Ducale)

Chair: Michele Saviano		
09:00	PL3	Flavio Bonati Memorial Lecture <u>Paul J. Dyson</u> , Ecole Polytechnique Fédérale de Lausanne <i>The development of organometallic anticancer drugs based on ruthenium</i>
10:00	OC11	<u>Alberto Credi</u> , Massimo Baroncini, Benoit Colasson, Marcello La Rosa, Giulio Ragazzon, Serena Silvi, Margherita Venturi <i>Photoresponsive molecular devices and materials</i>
10:15	OC12	<u>Stefano Stagni</u> , Valentina Fiorini, Massimiliano Massi <i>Design to application: the development of tetrazolate-based luminescent metal complexes</i>
10:30	OC13	<u>Pietro Tagliatesta</u> <i>Synthesis and Characterization of New Ferrocene, Porphyrin and C₆₀ Triads, Connected by Triple Bonds</i>
10:45	OC14	<u>Claudia Graiff</u> , Alessia Bacchi, Stefano Canossa, Paolo Pelagatti, Lara Righi, Giovanni Predieri, Gabriele Manca, Carlo Mealli <i>Structural investigations on the behavior of methylene blue towards transition chlorometallates</i>
11:00	Coffee break	

	Chair: Alberto Credi	
11:30	KN3	<u>Pierluigi Barbaro</u> <i>Advancements in sustainable continuous flow processes for the fine chemical synthesis</i>
12:00	OC15	B. Chiavarino, <u>M. E. Crestoni</u> , S. Fornarini <i>Gas-phase reactivity and spectroscopy of ionic intermediates involved in NO binding and delivery</i>
12:15	OC16	<u>Laura Calvillo</u> , Marco Favaro, Mattia Cattelan, Stephen Price, Andrea E. Russell, Stefano Agnoli, Gaetano Granozzi <i>In situ study on highly performing graphene quantum dots-MoS_x nanohybrids for the hydrogen evolution reaction (HER)</i>
12:30	OC17	<u>Iacopo Ciabatti</u> , Enrico Cattabriga, Cristina Femoni, Maria Carmela Iapalucci, Giuliano Longoni and Stefano Zacchini <i>New Platinum Carbonyl Nanoclusters</i>
12:45	OC18	<u>Pierluigi Plastina</u> , Iolinda Aiello, Alessandra Crispini, Mauro Ghedini, Nicolas Godbert, Massimo La Deda <i>Novel β-aminoketonate complexes of Iridium(III): synthesis and characterization</i>
13:00	Pranzo	
14:30	Sessione Poster Coffe break	
	Chair: Gaetano Granozzi	
17:00	KN4	<u>Silvia Gross</u> <i>Pursuing crystallisation at very low temperature: wet-chemistry and colloidal routes for the synthesis of mono- and polymetallic crystalline inorganic nanostructures</i>
17:30	KN5	<u>Antonella Accardo</u> <i>Supramolecular gadolinium complexes as contrast agents in Magnetic Resonance Imaging</i>
18:00	Assemblea della Divisione di Chimica Inorganica della SCI	
20:30	Plenary and Key-notes dinner	

Venerdì 11 settembre (Sala della Muta, Palazzo Ducale)

	Chair: Roberto Gobetto	
09:00	PL4	Paolo Chini Memorial Lecture <u>Antonio Togni</u> , Swiss Federal Institute of Technology, Switzerland <i>The Trifluoromethyl Group in Catalysis and Organometallic Chemistry</i>
10:00	OC19	<u>M. Benedetti</u> , F. De Castro, C.R. Girelli, D. Antonucci, P. Papadia, F. Capitelli and F.P. Fanizzi <i>¹⁹⁵Pt NMR chemical shift as a function of the coordinated halidos ionic radii overall sum</i>
10:15	OC20	<u>Barbara Chiavarino</u> , Maria Elisa Crestoni, Simonetta Fornarini, Jean-Yves

		Salpin <i>Interaction of cisplatin with 5'-dGMP: a combined IRMPD and theoretical study</i>
10:30	OC21	<u>Alessandro Caselli</u> , Giorgio Tseberlidis, Daniele Valcarengi, Emma Gallo, Monica Dell'Acqua, Giorgio Abbiati <i>Well defined [Silver(I)(Pyridine-Containing Ligand)] Complexes</i>
10:45	OC22	<u>Paolo Pelagatti</u> , Alessia Bacchi, Davide Capucci, Anna Gatti, Cecilia Loffi, Marianna Pioli, Dominga Rogolino, Vincenzo Verdolino <i>A journey into the coordination properties of naphthalimides toward the (p-cymene)Ru and Cp*Ru fragments</i>
11:00	Coffee break	
	Chair: Francesco Fanizzi	
11:30	KN6	<u>Antonino Martorana</u> , Chiara Aliotta, Marianna Gambino, Francesco Giannici, Alessandro Longo <i>Structure, conductivity and reactivity in materials for solid oxide fuel cells</i>
12:00	OC23	<u>Lucia Tonucci</u> , Nicola d'Alessandro, Krystel Di Pietrantonio <i>Catalytic activity of green metal nanoparticles</i>
12:15	OC24	<u>Elio Giamello</u> , Maria Cristina Paganini, Mario Chiesa, Chiara Gionco, Stefano Livraghi <i>Band gap engineering in semiconducting and insulating oxides</i>
12:30	OC25	<u>Andrea Giacomo Marrani</u> , Marco Carboni, Daniela Giacco, Sergio Brutti <i>Surface reactivity of carbonaceous cathodes in Li-O₂ batteries: an ex-situ XPS investigation</i>
12:45	OC26	<u>Monica Pica</u> , Morena Nocchetti, Anna Donnadio, Ferdinando Costantino, Pier Luigi Gentili, Mario Casciola <i>Zirconium phosphate/silver chloride composites: synergistic effects for the photocatalytic degradation of organic dye pollutants</i>
13:00	Pranzo	
14:30	Sessione Poster Coffe break	
	Chair: Francesco Fanizzi	
16:30	KN7	<u>Laura Prati</u> <i>Carbon material functionalisation as a versatile tool for different catalytic applications</i>
17:00	Gita sociale	
20:30	Cena sociale	

Sabato 12 settembre (*Sala della Muta, Palazzo Ducale*)

	Chair: Claudio Pettinari	
09:00	PL5	Unicam Chemistry Lecture <u>Omar M. Yaghi</u> , University of California-Berkeley <i>The Invention of New Materials</i>

10:00	OC27	<u>Andrea Rossin</u> , Samuele Staderini, Giulia Tuci, Giuliano Giambastiani and Maurizio Peruzzini <i>Zinc coordination polymers containing the isomeric forms of thiazolyl benzoic acid: synthesis and applications in ion sensing</i>
10:15	OC28	<u>Silvia Carlotto</u> , Maurizio Casarin, Arianna Lanza, Fabrizio Nestola, Luciano Pandolfo, Claudio Pettinari, Rebecca Scatena <i>Reaction of Copper(II) Chloroacetate with Pyrazole. Synthesis of a 1D Coordination Polymer and Unexpected Dehydrochlorination Reaction</i>
10:30	OC29	A. Giordana, <u>E. Priola</u> , E. Bonometti, L. Operti, E. Diana <i>Crystal engineering of non-centrosymmetric systems</i>
10:45	OC30	<u>Morena Nocchetti</u> , Riccardo Vivani, Ferdinando Costantino, Oriana Piermatti, Luigi Vaccaro <i>Zirconium Carboxy-aminophosphonate Nanosheets as Versatile Support for Metallic Nanoparticles</i>
11:00	Coffee break	
	Chair: Valerio Zanotti	
11:30	KN8	<u>Rossana Galassi</u> <i>Rationalization of monomer/cyclotrimer chemistry of coinage metals azolate compounds leading to unexpected biological properties</i>
12:00	OC31	Annarita Noschese, Antonio Buonerba, Carmine Capacchione, Stefano Milione, Alfonso Grassi <i>Nitrobenzene Reduction with AuNPs supported onto a polymeric matrix</i>
12:15	OC32	<u>Silvia Villa</u> , Paola Riani, Emanuele Magi, Fabio Canepa <i>Capture of heavy metals by thiol functionalized magnetic nanoparticles using a system of permanent magnets</i>
12:30	OC33	<u>Iole Venditti</u> , Laura Bracci, Alessandra Rossi, Chiara Battocchio, Francesco Porcaro, Giovanni Polzonetti, Laura Fontana, Giovanna Testa, Maria Vittoria Russo, Ilaria Fratoddi <i>Functionalized gold nanoparticles for drug delivery: Au3MPS@Dexamethasone as case of study</i>
12:45	OC34	<u>Anna Donnadio</u> , Morena Nocchetti, Riccardo Vivani, Ferdinando Costantino, Marco Taddei, Mario Casciola <i>Synthesis, Crystal Structure, and Proton Conductivity of 1D, 2D and 3D Zirconium Phosphonates Based on Glyphosate and Glyphosine</i>
13:00	Conclusioni Cerimonia di chiusura	

Elenco posters

- P1** Davide Balestri, Davide Capucci, Paolo Pelagatti, Alessia Bacchi, Nicola Demitri
MOFs as crystalline sponges for trapping nicotine and other APIs
- P2** Francesco Bartoli, Carla Bazzicalupi, Andrea Bencini, Paolo Foggi, Laura Bussotti, Agnese Magnani, Barbara Valtancoli
Selective fluorescence sensing of uracil-containing molecules with a dizinc(II) complex
- P3** Alberto Bucci, Gabriel Menendez Rodriguez, Gianfranco Bellachioma, Cristiano Zuccaccia, Alceo Macchioni
*Comparing the catalytic activity of Cp*Ir catalysts with bpy and dpa: insights into the mechanism of water oxidation driven by CAN*
- P4** Rossana Galassi, Oumarou Camille Simon, Vladimir Nesterov, Alceo Macchioni, Cristiano Zuccaccia, Mohammad A. Omary
Columnar stacking materials based on donor/acceptor complexes of tetrathiofulvalene / coinage-metal metallocycles
- P5** Rossana Galassi, Oumarou Camille Simon, Anna Teresa Ramadori, Stefania Pucciarelli, Albana Hisy, Manuela Iezzi, Valentina Gambini, Martina Tilio, Cristina Marchini, Augusto Amici
Azolate/phosphane Gold(I) compounds in antiproliferative therapy: a new frontier for the azolate gold(I) chemistry
- P6** Andrea Cingolani, Cristiana Cesari, Rita Mazzoni, Stefano Zacchini, Valerio Zanotti
A class of novel iron N-heterocyclic carbene complexes for redox catalytic reactions
- P7** Francesca Condello, Agnese Petrini, Jessica Palmucci, Riccardo Pettinari, Fabio Marchetti, Claudio Pettinari, Paul J. Dyson
Bioactivity of Curcuminoids in Half-Sandwich Ru(II), Rh(III) and Ir(III) Complexes: benefits from cooking to medicine
- P8** D. Corinti, C. Coletti, N. Re, B. Chiavarino, M. E. Crestoni, S. Fornarini
Cisplatin reactions with model biological ligands monitored by IR multiphoton dissociation spectroscopy
- P9** Massimiliano Aschi, Marcello Crucianelli, Fabio Marchetti, Claudio Pettinari, Riccardo Pettinari, Giovanni Piacente
A DFT Study on the stability of novel polynuclear oxovanadium based complexes with acylpyrazolone donor ligands
- P10** Federica De Castro, Michele Benedetti¹, Alessandro Romano, Tiziano Verri, Marco Lelli, Norberto Roveri and Francesco Paolo Fanizzi
Hydroxyapatite nanocrystals and controlled delivery of cisplatin derivatives
- P11** S. Delsante, G. Borzone, R. Novakovic
Synthesis and thermodynamics of Ag–Cu nanoparticles
- P12** Serena De Negri, Pavlo Solokha, Riccardo Freccero, Davide M. Proserpio, Adriana Saccone
Crystal structure and chemical bonding of R₂MGe₆ compounds (R = rare earth metal; M = Mg, Pd)
- P13** Assunta De Nisi, Marco Leonzio, Giorgio Sartor, Christian Bergamini, Romana Fato, Natalia Calonghi, Marco Bandini¹ and Magda Monari
New alkynyl-gold(I) complexes featuring anti-cancer activity

- P14** Carlo Diaferia, Eliana Gianolio, Marilisa Leone, Flavia Mercurio, Giancarlo Morelli, Antonella Accardo
Aromatic Peptide Conjugates as potential MRI contrast agents
- P15** Eliano Diana, Emanuele Priola
Solid state luminescence of d^{10} Hg(II) complexes: an integrated experimental and periodic computational approach
- P16** Giuseppe Di Natale, Alessandro Sinopoli, Giuseppe Pappalardo, Imre Sovago
Copper(II) interaction within the N-Terminal domain using a molecular mimic of an A β (1-16) dimer: new insights into the coordination properties of oligomeric A β .
- P17** Anna Donnadio, Monica Pica, Mario Casciola
Fluoroalkyl Zirconium Phosphates as nanofillers of PFSA based composite membrane for fuel cell applications
- P18** Mohamed A. EL-Atawy, Francesco Ferretti, Fabio Ragaini
Synthesis of Some Pyrrole Derivatives by Reductive Cyclization of Nitrodiene Catalyzed by Palladium Complexes and with Carbon Monoxide as the Reductant
- P19** Francesco Ferretti, Lilian Ansaloni, Fabio Ragaini
Ferrite Magnetic Nanoparticle for the Recycle of Palladium/Phenanthroline Catalytic Systems
- P20** Rossana Galassi, Alfredo Burini, Vladimir Nesterov, Mohammad A. Omary, Oumarou Camille Simon
Homo- and Heterotrinnuclear cyclic complexes of the 11th group metal ions: fifteen years of a golden chemistry
- P21** A. Giordana, E. Priola, E. Bonometti, L. Operti, E. Diana
Crystal engineering of non-centrosymmetric systems
- P22** Roberto Gobetto, Marcello Baricco, Michele R. Chierotti, Federico Franco, Carlo Nervi, Federico M. Paruzzo, Anna R. Wolczyk
Synthesis and characterization of novel hydrogen storage materials
- P23** Valentina Grazianni, Cecilia Coletti, Nazzareno Re, Alessandro Marrone
Activation and Reactivity of a Bispidine Analogue of Cisplatin: A Theoretical Investigation
- P24** Lucia Fagiolari, Antonio Scafuri, Ferdinando Costantino, Riccardo Vivani, Alceo Macchioni
An Efficient and Recyclable Water Oxidation Catalyst Obtained by "Diluting" Ir(III) into a ZnAl LDH Structure
- P25** Ilaria Corbucci, Kevin Ellingwood, Pier Luigi Gentili, Alceo Macchioni
Photocatalytic Water Oxidation with Iridium Catalysts Under Visible Light
- P26** Danilo Milardi, Irene Monaco, Anna Maria Santoro, Valeria Lanza, Flora Tomasello, Giuseppe Pappalardo, Agata Graziella Copani, Enrico Rizzarelli
Copper and proteasome: common underlying mechanisms for cancer and neurodegeneration
- P27** Marco Monticelli, Cristina Tubaro, Stéphane Bellemin-Laponnaz
Bidentate heteroditopic diNHCs: an original class of ligands for transition metal complexes

- P28** Luca Nencini, Claudio Cometto, Federico Franco, Fabrizio Sordello, Claudia Barolo, Roberto Gobetto, Claudio Minero, Carlo Nervi
Non classical diimine ligands for molecular catalysts based on VI Group transition metals for electroreduction of CO₂
- P29** Jessica Palmucci, M.F.C. Guedes da Silva, F. Marchetti, C. Pettinari, R. Pettinari, L. M. D. R. S. Martins, K. T. Mahmudov, G. Lupidi, D. Petrelli, A.J.L. Pombeiro
Synthesis, Characterization, Catalytic Activity and Biological of New Arylhydrazones of Barbituric Acid Complexes with Co(II), Cu(II) and Ag(I)
- P30** Luciano Pandolfo, Arianna Lanza, Fabrizio Nestola, Claudio Pettinari, Rebecca Scatena, Federico Zorzi
Porous coordination polymers based on the trinuclear triangular [Cu₃(μ₃-OH)(pz)₃] (pz = pyrazolate) moiety and bicarboxylate ions
- P31** G. Pappalardo, A. Sinopoli, A. Giuffrida, M.L. Giuffrida, M.F. Tomasello, F. Attanasio, M. Leone, F.A. Mercurio, M. Saviano, F. Caraci, A. Copani, E. Rizzarelli
Inhibitor of Alzheimer's amyloid-β peptide aggregation and neurotoxicity by the Trehalose conjugated β-sheet breaker peptide Ac-LPFFD-Th
- P32** Maura Pellei, Marika Marinelli, Cristina Marzano, Valentina Gandin, Marina Porchia, Francesco Tisato and Carlo Santini
Novel symmetrical and non-symmetrical 11th group-NHC complexes: synthesis, cytotoxicity and solution behavior
- P33** Agnese Petrini, Francesca Condello, Jessica Palmucci, Giulio Lupidi, Riccardo Pettinari, Fabio Marchetti, Claudio Pettinari and Paul J. Dyson
Synthesis, Characterization and Bioactivity of Novel Pentamethylcyclopentadienyl Rh(III) and Ir(III) Complexes Containing Dibenzoylmethane
- P34** M. Porchia, F. Tisato, C. Marzano, M. Pellei, C. Santini, V. Gandin
[HB(pz)₃]Ag(PR₃) complexes as thioredoxine reductase-targeted antiproliferative agents
- P35** Giovanni Predieri, Laura Bergamonti, Claudia Graiff, Clelia Isca, Pier Paolo Lottici
Wood and Paper protection with hybrid inorganic-organic polymers
- P36** Fabio Ragaini, Francesco Ferretti, Mohamed A. EL-Atawy
Phenanthrolines: a Non-Chromatographic Purification Method
- P37** Paola Riani, Silvia Villa, Fabio Canepa
Synthesis and characterization of Co-carbides particles
- P38** G. Roselli, M. Minicucci, G. Di Girolami, V. Corradetti, P. Cinaglia
New findings and analyses with non-invasive techniques on paintings by Pietro Alamanno (15th century) held at the Ascoli Piceno Pinacotheca
- P39** Antonio Roviello, Fabio Borbone, Barbara Panunzi, Stefano Piotta Piotta, Rafi Shikler, Angela Tuzi
New photoluminescent Zn(II) complexes with O,N,N ligands containing substituted benzo-1,3-diazole heterocycles
- P40** Carlo Santini, Maura Pellei, Valentina Gandin, Francesco Tisato, Alessandro Dolmella, Cristina Marzano, Marco Giorgetti, Marika Marinelli and Marina Porchia
Copper(I) complexes with homoscorpionate tris(azolyl)borate and auxiliary monodentate phosphine ligands: synthesis and in vitro and in vivo Anticancer Activity

- P41** Paolo Sgarbossa, Andrea Biffis, Cristina Tubaro, Daniele Vicenzi, Riccardo Zecchin
Diisocyanide Pt(II) and Au(I) Complexes: Catalytic Activity and Reaction with Amines
- P42** Augusto Tassan, Mirto Mozzon, Giacomo Facchin
Synthesis and ¹³C {¹H}-NMR Spectroscopy Characterization of the Pt(0) Triangulo-Cluster Derivative [Pt₃(CO)₃(PPh₂Np)₃]
- P43** I. Tommasi, C. Annese, L. D'Accolti, C. Fusco, A. D. Pedullà
Unexpected 2-ethyl-functionalisation of 1,3-dimethylimidazol-2-ylidene with dimethylcarbonate: Use of the reaction system in organocatalysis
- P44** Iole Venditti, Fabio Sciubba, Maurizio Delfini, Chiara Battocchio, Giovanni Polzonetti, Laura Fontana, Giovanna Testa, Maria Vittoria Russo¹, Iliara Fratoddi
Gold and silver nanoparticles conjugated with Rhodamine B isothiocyanate: synthesis and depth characterization
- P45** Riccardo Vivani, Monica Pica, Anna Donnadio, Elisabetta Troni, Sacha Fop, Mario Casciola
Unusual behaviour of nanocrystalline zirconium phosphates
- P46** G. Valente, N. Depalo, I. de Paola, R. M. Iacobazzi, N. Denora, V. Laquintana, R. Comparelli, E. Altamura, T. Latronico, M. Altomare, E. Fanizza, M. Striccoli, A. Agostiano, M. Saviano, A. Del Gatto, and M. L. Curri and L. Zaccaro
Integrin Targeting with Peptide Bioconjugated Nanocrystalline Heterostructures: a Theranostic Prospect
- P47** Emanuele Priola, Elisabetta Bonometti, Eliano Diana
In situ generation of a family of substituted thioureas-Cadmium thiocyanate coordination polymers: a crystal engineering study for new topologies and properties
- P48** Nello Mosca, Nertil Xhaferaj, Claudio Pettinari, Fabio Marchetti, Riccardo Pettinari
Novel Coordination Frameworks Based on Polytopic Heteroaromatic Nitrogen and Carboxylate Ligands

Plenary Lectures

PL1

Interface Science of Soft Matter Photovoltaics

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The ability to fabricate molecularly tailored interfaces with nanoscale precision offers means to selectively modulate charge transport, molecular assembly, and exciton dynamics at hard matter-soft matter and soft-soft matter interfaces. Such interfaces can facilitate transport of the “correct charges” while blocking transport of the “incorrect charges” at the electrode-active layer interfaces of organic photovoltaic cells. This interfacial tailoring can also suppress carrier-trapping defect densities at interfaces and stabilize them with respect to physical/thermal de-cohesion. For soft matter-soft matter interfaces, interfacial tailoring can also facilitate exciton scission and photocurrent generation in such cells. In this lecture, challenges and opportunities in organic photovoltaic interface science are illustrated for four specific and interrelated areas of research: 1) controlling charge transport across hard matter(electrode)-soft matter interfaces in organic photovoltaic cells, 2) controlling charge transport by specific active layer nano/microstructural organization in the bulk active material and at the electrodes, 3) controlling exciton dynamics and carrier generation at donor-acceptor interfaces in the active layer, 4) designing transparent conducting oxide electrodes with improved properties. It will be seen that such rational interface engineering along with improved bulk-heterojunction polymer structures guided by theoretical/computational analysis affords exceptional fill factors, solar power conversion efficiencies greater than 10%, and enhanced cell durability.

PL2

Interfaces at the nanoscale: a new paradigm in catalysis

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Surface science studies are clearly delineating a consistent paradigm pointing to the use of interfaces as an effective tool for stabilizing highly active chemical species. So far the most commonly used approach consists of supporting oxides on metals since it is possible to take advantage of the electronic interactions at the interface that can increase the adhesion of the oxide or modify its electronic properties. However, an alternative path, thus far less explored, is the formation of oxide-on-oxide interfaces [1], or complex heterostructures between 2D solids such as graphene and transition metal dichalcogenides [2]. In the past few years, we have tackled the study of several types of model systems constituted by ultrathin oxides films supported on metals. As outlined by the exemplary case of the NiO/Pd(100), these systems exhibit rather unusual structures and are quite interesting because of their enhanced chemical activity, which directly stems from the special electronic properties of the metal/oxide interface [3,4].

More recently, we have investigated nanointerfaces between reducible oxides ($\text{CeO}_x/\text{TiO}_2$ and VO_x/TiO_2) [5,6,7], revealing the formation of exotic nanostructures that exhibit outstanding reactivity, especially in the low temperature conversion of alcohols. The body of this experiment work helps to substantiate a new paradigm in nanocatalysis, which identifies the common origin of the high chemical activity in the peculiar properties of interfaces that can stabilize unusual structures or highly active chemical species either by electronic hybridization ($\text{CeO}_x/\text{TiO}_2$) or by charge transfer (VO_x/TiO_2). Interestingly, the concepts developed by model studies in ultra high vacuum conditions have been exploited for the preparation of titania@ceria core@shell nanoparticles, which resulted to be very promising catalysts with biomimetic activity [8].

- [1] L. Artiglia, S. Agnoli, G. Granozzi *Coord. Chem. Rev.*, doi:10.1016/j.ccr.2014.12.015 (2015).
- [2] M. Cattelan et al., *Chem. Mater.* 21 (2015) 4105.
- [3] S. Agnoli et al., *J. Phys. Chem. B* 109 (2015) 17197.
- [4] S. Agnoli et al., *J. Phys. Chem. C* 111 (2007) 19066.
- [5] L. Artiglia, S. Agnoli et al., *J. Am. Chem. Soc.* 135 (2013) 17331.
- [6] L. Artiglia, S. Agnoli et al., *ACS Catalysis* 4 (2014) 3715.
- [7] S. Agnoli et al., *Nanoscale* 6 (2014) 800.
- [8] L. Artiglia, S. Agnoli et al., *ACS Appl. Mater. Interfaces* 6 (2014) 20130.

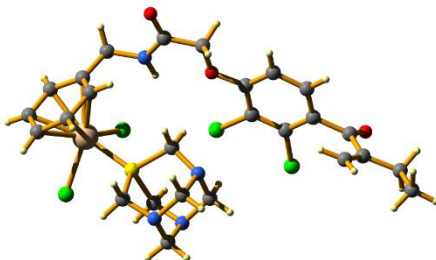
PL3

The development of organometallic anticancer drugs based on ruthenium

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The presentation will focus on our research on ruthenium-based organometallic compounds that exhibit selective anticancer activity against highly invasive tumors, and potentially overcome certain limitations of present metal-based and organic anticancer drugs. In particular, drug resistance is a major problem and is known to be the consequence of a multitude of factors such as reduced drug uptake, increased efflux and drug inactivation by intracellular thiol-containing biomolecules. We show that inorganic-organic hybrid systems are able to overcome certain types of drug resistance mechanisms and therefore act in a targeted fashion. The study of these compounds in combination with clinically approved compounds is also described. The characterization and activity of these complexes and drug combinations including drug-drug interactions will be discussed and their mechanism of action highlighted [1].



In addition, the development and use of organometallic compounds in combination with hyperthermia will also be described [2]. Hyperthermia is used as an adjuvant with chemotherapy and is a highly promising approach for the treatment of certain chemoresistant cancers and the new organometallic compounds appear to offer superior options to the current compounds used.

[1] B. S. Murray, M. V. Babak, C. G. Hartinger, P. J. Dyson, *Coord. Chem. Rev.*, DOI: <http://dx.doi.org/doi:10.1016/j.ccr.2015.06.014>.

[2] C. M. Clavel, P. Nowak-Sliwinska, E. Păunescu, A. W. Griffioen, P. J. Dyson, *Chem. Sci.* 6 (2015) 2795.

PL4

The Trifluoromethyl Group in Catalysis and Organometallic Chemistry

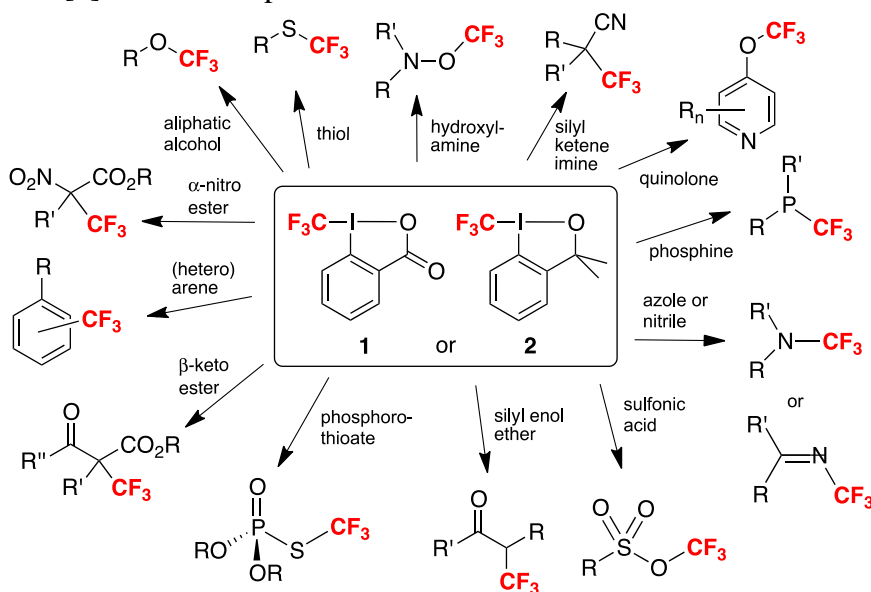
Antonio Togni

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The lecture will focus on selected examples of trifluoromethylation reactions carried out with hypervalent iodine reagents of type **1** and **2** [1]. These transformations, upon which an intact CF₃ group may be transferred to a large variety of substrates, are catalyzed or assisted by Brønsted and Lewis acids, or by a number of transition-metal complexes.

Thus, *N*- and *P*-trifluoromethylations of benzimidazole or both primary and secondary phosphines, respectively, are used for the preparation of corresponding carbene ligands [2] and novel *P*-stereogenic phosphines [3] for applications in homogeneous catalysis.

Structural modifications and modes of activation of the reagents as well as mechanistic insights deriving from both experiments and quantum-chemical calculations [4] will also be presented.



[1] For a recent comprehensive review, see: J. Charpentier, N. Früh, A. Togni, *Chem. Rev.* 115 (2015) 650, and references cited therein (Open access: <http://pubs.acs.org/doi/full/10.1021/cr500223h>)

[2] P. S. Engl, R. Senn, E. Otth, A. Togni, *Organometallics* 34 (2015) 1384.

[3] R. Schwenk, A. Togni, *Dalton Trans.* (2015), DOI: 10.1039/C5DT02019K.

[4] O. Sala, H. P. Lüthi, A. Togni, M. Iannuzzi, J. Hutter, *J. Comput. Chem.* 36 (2015) 785.

PL5

The Invention of New Materials

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Metal-organic frameworks (MOFs) represent an extensive class of porous crystals in which organic ‘struts’ are linked by metal oxide units to make open networks. The flexibility with which their building units can be varied and their ultra-high porosity (up to 10,000 m²/g) have led to many applications in gas storage and separations for clean energy. This presentation will focus on (1) how one can design porosity within MOFs to affect highly selective separations (carbon dioxide), storage (hydrogen and methane) and catalysis, and (2) a new concept involving the design of heterogeneity within crystalline MOFs to yield sequences that code for specific separations and chemical transformations.

Key Notes

KN1

Anilate-based Functional Molecular Materials with Conducting and Magnetic Properties

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Molecular materials showing electrical conductivity and/or magnetic properties are of great interest in material science for their academic interest as well as for their potential applications in the post-silicon era of molecular electronics.

In the search for new functional molecular materials whose physical properties can be easily tuned by simple changes on the molecular structures of their building units, we have designed and synthesized a family of paramagnetic metal complexes of general formula $[M^{III}(X_2An)_3]^{3-}$ ($M^{III} = Cr, Fe$; $X = Cl, Br, I, H, Cl/CN$; $An = 2,5$ -dihydroxy-1,4-benzoquinone) [1-3]. These metal complexes are valuable building blocks for the preparation of functional materials, such as molecule-based ferrimagnets and magnetic molecular conductors, where the nature of the substituent atom play a key role in determining their physical properties [4-6]. Here we report the synthesis and the full characterization of these metal complexes as well as the synthesis and characterization of a novel family of molecular ferrimagnets formulated as $A[Mn^{II}Cr^{III}(X_2An)_3]$ ($A = (n-Bu)_4N^+, [(phen)_3(H_3O)]^+$, $X = Cl, Br, I$). In this family, a simple change of the substituent atom (X) on the bridging ligand allows for a fine tuning of the magnetic properties: the ordering temperature increases from 5.5 to 6.3, 8.2 and 11.0 K for $X = Cl, Br, I, H$, respectively [4]. Furthermore, by combining the paramagnetic metal complex $[Fe(Cl_2An)_3]^{3-}$ with the organic donor BEDT-TTF (bis-ethylenedithio-tetrathiafulvalene) and its chiral derivatives (*S,S,S,S*)- and (*R,R,R,R*)-TM-BEDT-TTF via electrocrystallization, two novel families of paramagnetic molecular conductors have been obtained. The crystal structures and the physical properties of these magnetic/conducting hybrid systems will be also reported in this communication [5-6].

- [1] M. Atzori et al., *Dalton Trans.* 43 (2014) 7006.
- [2] M. Atzori et al., *Cryst. Growth Des.* 14 (2014) 5938.
- [3] M. Atzori et al., *Dalton Trans.* 2015, in press.
- [4] M. Atzori et al., *Inorg. Chem.* 52 (2013) 10031.
- [5] M. Atzori et al., *Inorg. Chem.* 53 (2014) 7028.
- [6] M. Atzori et al., *Inorg. Chem.* 54 (2015) 3643.

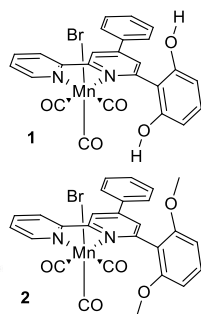
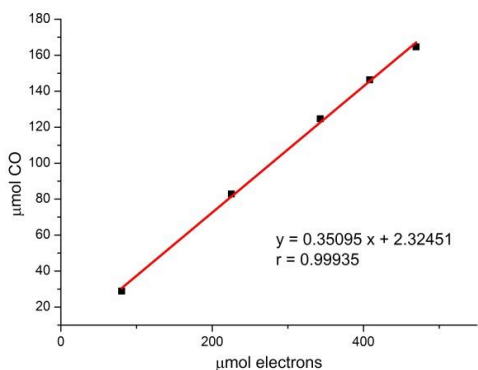
KN2

Transition Metal Complex Catalysts for the Electrochemical Reduction of CO₂

Carlo Nervi, Roberto Gobetto

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The conversion of CO₂ into valuable chemicals/fuels is a perfect way for approaching the contemporary challenges of green-house emission and depletion of fossil energy resources. The need for a radical breakthrough in energy supply technologies can be ideally pursued by the so-called “Solar Fuel” approach [1]. However, artificial photosynthesis of organic molecules is still far away from providing real-world solutions. One of the scientific challenges is to perform efficiently and selectively the multi-electron reduction of carbon dioxide. A convenient approach is to optimize separately the catalytic and light-harvesting properties. This is possible because the photocatalytic mechanism usually proceed via a reductive quenching pathway [2], i.e. the real catalyst is the reduced form produced in situ; thus the search of an efficient catalyst for CO₂ reduction and its study can be pursued using electrochemical techniques. In this presentation an overview of our and other recent advances in the use of organometallic complexes as catalysts for electrochemical CO₂ reduction will be illustrated. Analogies and differences among several transition metal complexes will be outlined, including the better known mechanism



based on Re(bpy) complexes, the effect of local proton sources on the Mn(bpy) complexes [3] as well as some outline on the use of earth-abundant transition metal complexes (Mo and W) [4] employed as redox catalysts for CO₂ electrochemical reduction.

- [1] J. Rongé, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordiga, J. A. Martens, *Chem.Soc.Rev.* 43 (2014) 7963.
[2] a) J. M. Saveant, *Chem. Rev.* 108 (2008) 2348; b) C. Costentin, M. Robert, J. M. Saveant, *Chem. Soc. Rev.* 42 (2013) 2423.
[3] F. Franco, C. Cometto, F. Ferrero Vallana, F. Sordello, E. Priola, C. Minero, C. Nervi, R. Gobetto, *Chem. Commun.* 50 (2014) 14670.
[4] a) F. Franco, C. Cometto, C. Garino, C. Minero, F. Sordello, C. Nervi, R. Gobetto, *Eur. J. Inorg. Chem.* (2015) 296; b) F. Franco, C. Cometto, F. Sordello, C. Minero, L. Nencini, J. Fiedler, R. Gobetto, C. Nervi, *ChemElectroChem.* (2015), DOI: 10.1002/celec.201500115

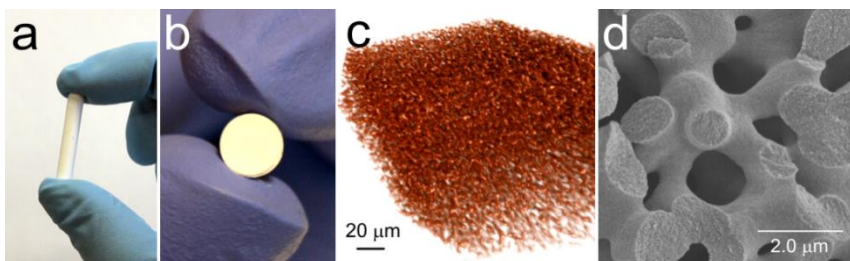
KN3

Advancements in sustainable continuous flow processes for the fine chemical synthesis

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Recent advancements in the field of new materials, catalysts and processes for the production of chemicals under continuous flow are presented with regard to synthetic strategies fulfilling the Principles of Green Chemistry. Two research lines are discussed: a) unconventional monolith catalysts with hierarchical porosity [1,2], b) one-pot conversion of plant biomass by bifunctional catalysts [3,4].



- [1] N. Linares, S. Hartmann, A. Galarneau, P. Barbaro, *ACS Catalysis* 2 (2012) 2194.
- [2] A. Sachse, N. Linares Perez, P. Barbaro, F. Fajula, A. Galarneau, *Dalton Trans.* 42 (2013) 1378.
- [3] C. Moreno-Marrodan, P. Barbaro, *Green Chem.* 16 (2014) 3434.
- [4] F. Liguori, C. Moreno-Marrodan, P. Barbaro, *ACS Catalysis* 5 (2015) 1882.

KN4

Pursuing crystallisation at very low temperature: wet-chemistry and colloidal routes for the synthesis of mono- and polymetallic crystalline inorganic nanostructures

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Pursuing crystallisation of inorganic nanostructures may enhance or even promote *ex-novo* functional properties such as, *inter alia*, superconductivity, catalytic or optical properties. In this framework, to achieve crystallisation through the use of low temperature and sustainable processes based on cheap and safe chemicals represents a challenging playground in modern inorganic chemistry [1, 2].

In these last years, we have developed in our group different low temperature ($T < 150^\circ\text{C}$) wet and green chemistry routes [3] to prepare different inorganic functional nanomaterials, ranging from i) ferrites [4], to manganites [5], to pure and doped ii) transition metal metal oxides [6-8], sulphides [9-10] and halogenides [11], to iii) metal/metal oxide nanocomposites [10]. The adopted wet chemistry routes are i) miniemulsions [3, 6-7, 9, 11,12], affording crystallisation in confined space and typically at room temperature, ii) coprecipitation combined with hydrothermal route [4-5] to 3) or iii) more classical colloidal routes [8, 10], as well as combination thereof. Recently, we are exploring the innovative combination of miniemulsion synthesis under hydrothermal treatment. The routes were optimised in order to pursue crystallisation of the targeted systems already at the low temperatures employed, and the synthetic optimisation was complemented by a multi-technique approach (based on the interplay among XAS, XPS, XRD and SAXS) implemented to follow, also in temperature and time-resolved mode, the evolution towards crystallisation of the targeted systems.

- [1] D. Cushing et al. *Chem. Rev.* 104 (2004) 3893.
- [2] J. Dahl et al. *Chem. Rev.* 17 (2007) 2228.
- [3] P. Dolcet, S. Gross et al., *J. Sol-Gel Sci. Technol.* 73 (2015) 591.
- [4] S. Diodati, S. Gross et al. *Nano Res.*, 7 (2014) 1027.
- [5] A. Minelli, S. Gross et al. submitted.
- [6] P. Dolcet, S. Gross et al. *J. Mater. Chem.* 22 (2012) 1620.
- [7] P. Dolcet, S. Gross et al. *Eur. J. Inorg. Chem.* 13 (2013) 2291.
- [8] A. Famengo, S. Gross et al. *Eur. J. Inorg. Chem.* (2009) 5017.
- [9] P. Dolcet, S. Gross et al. *Eur. J. Inorg. Chem.* 4 (2015) 706.
- [10] D. Camozzo, S. Gross et al. *J. Nanosci. Nanotech.* 6 (2006) 401.
- [11] P. Dolcet, S. Gross et al. *RSC Advances*, 5 (2015) 16302.
- [12] N. Heutz, P. Dolcet, S. Gross et al. *Nanoscale* 5 (2013) 10534.

KN5

Supramolecular gadolinium complexes as contrast agents in Magnetic Resonance Imaging

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Magnetic Resonance Imaging (MRI) is one of the most powerful and non-invasive techniques for medical diagnosis [1]. Currently, stable Gd(III)-poli(aminocarboxylate) complexes are widely used as contrast agents (CAs) in MRI. They are intravenously administered to patients, and by reducing the relaxation time of water protons presented in the effected tissues, they help to produce high quality images [2]. Although MRI gives very resolved images, due to its very low sensitivity, it needs high concentration (10^{-4} M) of contrast agents on the target organs. In the last years, several macromolecular or supramolecular systems such as dendrimers, polymers, gadofullerenes, gadonanotubes, micelles, liposomes and nanoparticles [3] have been proposed to reach the required local concentration of gadolinium complexes. In the present communication, novel supramolecular systems, based on diolein or phenylalanine homodimer (FF) will be proposed as potential MRI contrast agents.

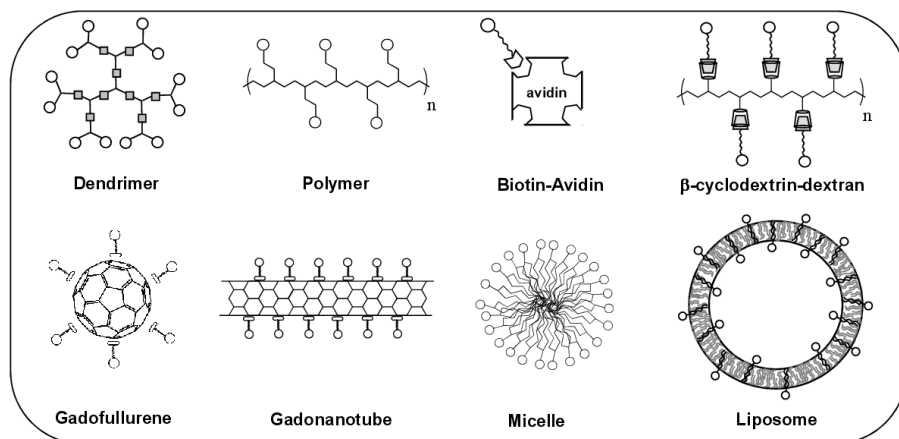


Figure 1. Schematic representation of macromolecular and supramolecular adducts derivatized with stable gadolinium complexes by covalent or non-covalent interactions between high molecular weight molecules and monomeric Gd(III) complexes.

[1] R. Weissleder, et al. *Molecular Imaging Radiology*, 316 (2001) 219.

[2] I. Toth, et al., In *The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging* (Eds.: A. E. Merbach, I. Toth), Wiley, Chichester 2001, pp. 45-119.

[3] A. Accardo, et al. *Coord. Chem. Rev.* 253 (2009) 2193.

KN6

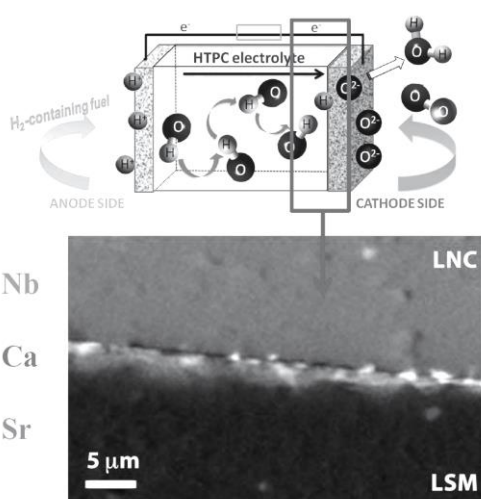
Structure, conductivity and reactivity in materials for solid oxide fuel cells

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Materials for Solid Oxide Fuel Cells (SOFC) are at the forefront of the research in solid state chemistry. Aiming at the design of electrolytes and electrodes with



improved properties and at the fabrication of robust and long-lived devices, the research efforts are addressed in particular to the development of solid state ionic conductors and oxide electrocatalysts with mixed ionic-electronic conduction. Among proton conductors, Y:BaZrO₃, Y:BaCeO₃, Ca:LaNbO₄ (LNC) and hybrid inorganic-organic conductors are most investigated, while electrolytes operating at intermediate temperature (700-800 °C) such as Gd- or Sm-doped cerium oxide are the most interesting oxide-ion conductors [1]. To improve the active region of contact between gas reactants,

electronic and ionic conducting phases, mixed ionic-electronic conducting (MIEC) materials, like La_{0.6}Sr_{0.4}MnO₃ (LSM) and La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ (LSCF) are today at the forefront of the research on electrodes. In the fabrication of devices, the issue of electrode-electrolyte compatibility, involving similarity of expansion coefficients and absence of interface reactions and/or cation interdiffusion, is essential [2]. Investigation of materials and assemblies for SOFC requires the complementary use of several experimental techniques; among them, X-ray spectroscopies, allowing to assess local structure and oxidation state, are essential to establish reliable structure-properties relationships.

[1] F. Giannici, G. Gregori, C. Aliotta, A. Longo, J. Maier, A. Martorana, *Chem. Mater.* 26 (2014) 5994.

[2] F. Giannici, G. Canu, M. Gambino, A. Longo, M. Salomé, M. Viviani, A. Martorana, *Chem. Mater.* 27 (2015) 2763.

KN7

Carbon material functionalisation as a versatile tool for different catalytic applications

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Carbon has a number of advantages over oxide supports such as stability in both acidic and basic environments and easy recovery of precious metal from deactivated catalyst by simply burning of the carbon. Moreover, carbon supports provide a nearly limitless palette of properties, which can be adjusted for specific applications. For example, adjusting the synthesis and processing conditions the pore sizes and surface areas of activated carbons can be controlled or the surface chemistry can be tailored to provide nucleation sites for metal particle growth or to adjust the concentration of acid/base/binding sites on the surface.

The presentation will focus on the use of different carbonaceous materials (active carbon, carbon nanotube, mesoporous carbon) as starting materials, which can be modified by the introduction of basic (N-containing) or acidic (COOH, S- or P-containing) groups. It will be shown that from a catalytic point of view the chemical nature of the groups is important as well as the number and the site of where the functionalization is introduced.

Biomass derived platform molecule transformations will be used to show how the different functionalities of the carbon supports can help in solving problems of selectivity and stability, which often affect the use of heterogeneous catalysts in biomass-derived materials.

KN8

Rationalization of monomer/cyclotrimer chemistry of coinage metals azolate compounds leading to unexpected biological properties

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Crystal structures of cyclic trinuclear complexes of the d^{10} monovalent coinage metals are fascinating for their elegant self-assembly, their supramolecular stackings based on non-classic chemical bonding, and for their remarkably - rich optoelectronic properties. The significance of this class of complexes embraces cross-sectional chemistry areas, including metalloaromaticity, metallophilic bondings, supramolecular assemblies, M-M bonded excimers and exciplexes, and host/guest chemistry. Moreover, this class of complexes are surprising for their fascinating luminescence properties and their acid/base behavior.[1] Their synthesis proceeds by combining azolate salts with coinage metal precursors, where the departure of a leaving group i. e. PPh_3 , Me_2S or the treatment with the M_2O affords to cyclic rearrangements. However, it is possible to modulate the syntheses and the properties of the final products by changing the substituents in the azolate. By introducing withdrawing groups such as CF_3 , NO_2 , Cl , CN , mononuclear derivatives can be obtained showing solubility properties in aqueous media: these latter azolate gold(I) phosphane derivatives were found to be good candidate for biological studies. Azolate gold(I) phosphane compounds resulted to be cytotoxic on the regards of many panel of cancer cells, in addition to cis-platin resistant cells.[2] Moreover, they inhibit pivotal enzymes, such as the seleno dependent ThioredoxinaReductase (TrxR),[2]and an enzyme involved in DNA synthesis such as DeHydroFolateReductase [3] On these new azolate gold(I) phosphane compounds different cell viability assays (MTT assays) were performed on a human *in vitro* model of HER2-overexpressing breast cancer: SKBR-3 cells. After this preliminary screening, the most promising and effective compounds were selected to extend the study on A17 cell line, a murine preclinical model of Basal Like Breast Cancer (BLBC).[4] In this seminar, the chemistry, the characterization and the biological studies with the aforementioned azolate compounds will be presented.

[1] R. Galassi et al. *Comm. Inorg. Chem.* (2015) submitted.

[2] R. Galassi et al., *Dalton Trans.* 41 (2012) 5307.

[3] R. Galassi et al., *Dalton Trans.* 44 (2015) 3043.

[4] M. Galiè et al., *Carcinogenesis* 11 (2005) 1868.

Oral Communications

OC1

Pincer 4-Functionalized 2-Aminomethylbenzo[*h*]quinoline Ruthenium Catalysts for Aldehyde / Ketone Reduction

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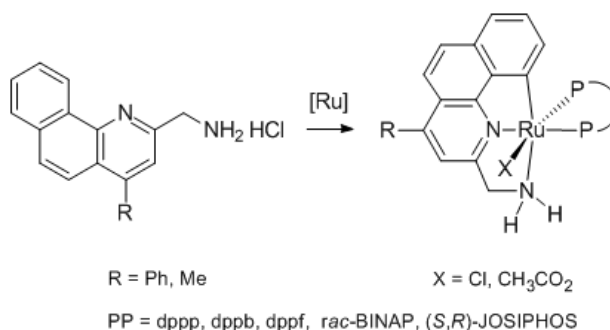
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²*Johnson Matthey Catalysis and Chiral Technologies, 28 Cambridge Science Park, Milton Road, Cambridge, CB4 0FP, United Kingdom*

Pincer complexes have attracted a great deal of attention in the last decade due to their good balance between stability and reactivity.^[1]

Ruthenium catalysts have successfully been applied in hydrogenation and transfer hydrogenation of carbonyl compounds for the synthesis of alcohols. On account of the operational simplicity and mild reaction conditions, transfer hydrogenation is being increasingly used in industrial plants and can be competitive with respect to hydrogenation. In addition to the asymmetric reduction, a great industrial concern is focused on robust achiral catalysts which can work with extremely low catalyst loading, aiming to replace the use of NaBH₄ and LiAlH₄, facilitating the work-up and reducing the side-products.

We report here the medium scale preparation of stable 4-functionalized-2-aminomethylbenzo[*h*]quinoline hydrochloride salts (HCNN^R·HCl) (R = Ph, Me) which are used for the synthesis of the pincer ruthenium complexes RuX(CNN^R)(diphosphine) (X = Cl, CH₃CO₂).



These pincer complexes are efficient catalysts^[2] for the transfer hydrogenation and hydrogenation of commercial-grade aldehydes and ketones with S/C up to 40000. Side reactions in the aldehyde reduction will also be discussed.

[1] C. Gunanathan, D. Milstein, *Chem. Rev.* 114 (2014) 12024.

[2] G. Chelucci, S. Baldino, W. Baratta, *Coord. Chem. Rev.* 300 (2015) 29.

OC2

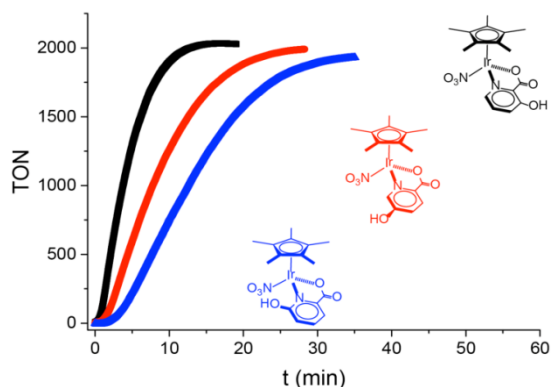
Positional Effect of a Hydroxyl Group on the Activity of Pyridyl-Carboxylate and –Aminidate Cp*Ir–Catalysts for Water Oxidation

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The development of a sustainable and renewable energy source is a crucial problem of our society because fossil fuels are rapidly depleting. A promising solution appears to be the realization of a photosynthetic apparatus aimed at producing solar fuels using electrons coming from the oxidation of water to O₂ [1]. The efficiency of such an apparatus seems to be limited by the still unsatisfactory performance of the catalytic pool for the oxidation of water.

Several transition metal complexes have been recently proposed as water oxidation catalysts (WOCs) [2] and those based on Cp*Ir (Cp*=1,2,3,4,5-pentamethylcyclopentadiene) have attracted much attention for their high, and easily tunable, activity and robustness.



Interestingly, Himeda and Papish [3,4] reported some Cp*Ir WOCs which contain proton-responsive ligands based on dihydroxy-2,2'-bipyridine derivatives. They showed that the introduction of the hydroxyl groups, in particular positions of the bipy rings, has a beneficial effect and strongly increases the catalytic activity of WOCs. This pushed us to undertake a systematic study on the introduction of

an –OH substituent in all positions of the py-ring of the [Cp*Ir(pic)NO₃] (where pic=2-pyridinecarboxylic acid) WOCs, previously reported by us [5], which are among the fastest catalysts reported so far, and in [Cp*Ir(pycxam)Cl] (where pycxam=2-pyridinecarboxamide). Indeed, the catalytic performances are dramatically affected by the presence and position of –OH (Figure, pH = 7 by phosphate buffer, C_{cat} = 5 μM, C_{NaIO₄} = 20 mM), by the pH of the medium and the nature of the sacrificial oxidant. The results will be discussed in this contribution.

[1] V. Balzani et al., *ChemSusChem*, 1 (2008) 26.

[2] P. Du et al., *Energy Environ. Sci.* 5 (2012) 8134.

[3] E. Fujita et al., *Phys. Chem. Chem. Phys.* 16 (2014) 11976.

[4] E.T. Papish et al. *Inorg. Chem.* 52 (2013) 9175.

[5] A. Bucci et al., *Organometallics* 31 (2012) 8071.

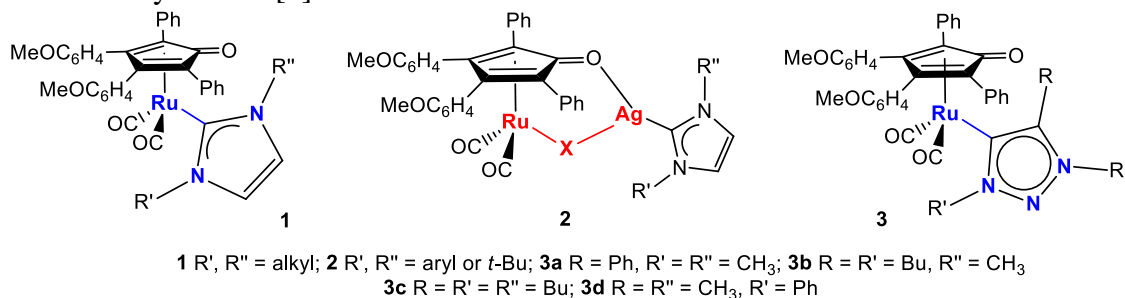
OC3

Synthesis of novel Ru N-Heterocyclic carbene complexes for bifunctional metal-ligand catalysis

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N-heterocyclic carbenes (NHC) are efficient ancillary ligands due to their strong coordination ability and their tuneable character which allows the control of the steric and electronic properties of the metal centre. [1] Herein we report the synthesis, characterization and catalytic applications of new carbonylic ruthenium complexes that combine tetraphenylcyclopentadienone and NHC ligands. Coordination of less bulky carbenes occurred through a straightforward transmetallation from the corresponding silver carbene intermediate to the dimeric precursor dicarbonyl(η^4 -3,4-bis-(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone), leading to the formation of a series of mononuclear complexes of type **1**. Conversely, sterically demanding imidazolium salts yielded the dinuclear Ru(II)-Ag(I) complexes of type **2**, in which the carbene remains coordinated to silver. [2] Furthermore, complexes of type **3** were obtained by replacing imidazolylidenes with triazolylidenes. [3]



The catalytic activity of the imidazolylidenes of type **1** and triazolylidenes (**3**) ruthenium complexes was investigated in homogeneous catalysis: the complexes **1a** (R' = R'' = CH₃), **1b** (R' = Bu, R'' = py) and **3a** were tested as catalyst precursors in transfer hydrogenation of 4-fluoroacetophenone and in the acceptorless dehydrogenation of benzyl alcohol.

[1] M.N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature* 510 (2014) 485.

[2] C. Cesari, S. Conti, S. Zacchini, V. Zanotti, M. C. Cassani, R. Mazzoni, *Dalton Trans.* 43 (2014) 17240.

[3] C. Cesari, R. Mazzoni, H. Muller-Bunz, M. Albrecht, *J. Organomet. Chem.* (2015) <http://dx.doi.org/10.1016/j.jorganchem.2015.02.022>

OC4

Metal complexes with di(N-heterocyclic carbene) ligands bearing an *ortho*-, *meta* or *para*-phenylene bridge

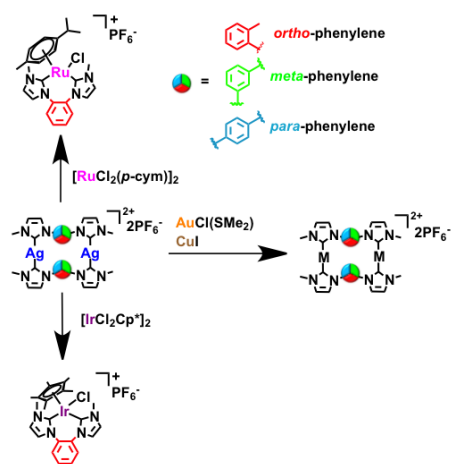
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Transition metal complexes with di(N-heterocyclic carbene) ligands (diNHC) in the coordination sphere have found application in many fields, spanning from photophysics to catalysis and medicine.¹ Generally the employed diNHCs have a flexible alkyl chain as bridging group between the carbene moieties.



In this work, we present our recent results on diNHC ligands with a rigid bridging group, namely *ortho*-, *meta*- and *para*-phenylene; in principle, the different geometry of functionalization of the aromatic ring could influence the bridging vs. chelating coordination of the dicarbene.^{2,3} Furthermore, the most frequent examples in the literature with this type of ligands, involve species with the *meta*-phenylene bridge; this ligand can act also as CCC-pincer as a consequence of the metalation of the phenylene bridge in the C2 position (with Ru(II), Ir(III) or Pt(II) centers).³

The dinuclear silver(I) complexes with bridging diNHC ligands can be easily obtained by reaction of the corresponding bis(imidazolium) salt with Ag₂O and we have investigated their ability to transfer the diNHC ligands to other metal centers. The reaction with Ir(III) and Ru(II) metal precursors is successfully only with the *ortho*-phenylene ligand and affords chelate complexes. By contrast, the reaction with the group 11 Cu(I) and Au(I) centers gives, as expected, dinuclear complexes with a structure similar to that of the starting silver precursors. Finally, the solid state structures and the luminescence properties of the Ag(I) and Au(I) complexes will be discussed and compared.

[1] A. Biffis et al., *Adv. Organomet. Chem.* doi:10.1016/bs.adomc.2015.02.002.

[2] A. Rit et al., *Organometallics* 30 (2011) 334.

[3] M. Raynal et al., *Organometallics* 28 (2009) 4028.

OC5

NHC Complexes of High Valent Niobium and Tantalum Halides

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Stefano Zacchini³

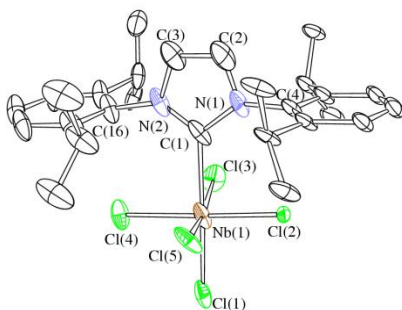
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Despite the outstanding properties that *N*-heterocyclic carbene ligands (NHC) may confer to the relevant metal complexes, the chemistry of NHC ligands has primarily focused on low and medium valent metals, while the isolation of derivatives of high valent metals is a harder task. This is particularly true for the halides of high oxidation state transition elements, due to the extreme moisture sensitivity usually exhibited by the related reaction systems [1].

We have synthesized a series of coordination adducts of MX_5 ($\text{M} = \text{Nb, Ta}$; $\text{X} = \text{F, Cl, Br}$), NbOF_3 and NbOX_2 ($\text{X} = \text{Cl, Br}$) with bulky, stable NHC ligands. Rare examples of crystallographic characterization of Nb(Ta)-NHC frames have been provided [2]. Moreover, DFT studies have been extensively carried out in order to shed light on mechanistic and structural features, the latter contributing to the knowledge of the yet poorly investigated high-valent metal-NHC bonding systems. A view of the X-ray structure of $\text{NbCl}_5(\text{Ipr})$ is shown in the Figure (displacement ellipsoids are at the 30% probability level).



[1] C. A. Dodds, M. D. Spicer and T. Tuttle, *Organometallics* 30 (2011) 6262.

[2] M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni and S. Zacchini, *Chem. Commun.* 50 (2014) 4472.

OC6

A coordination-driven pocket as nanoreactor and nanovessel

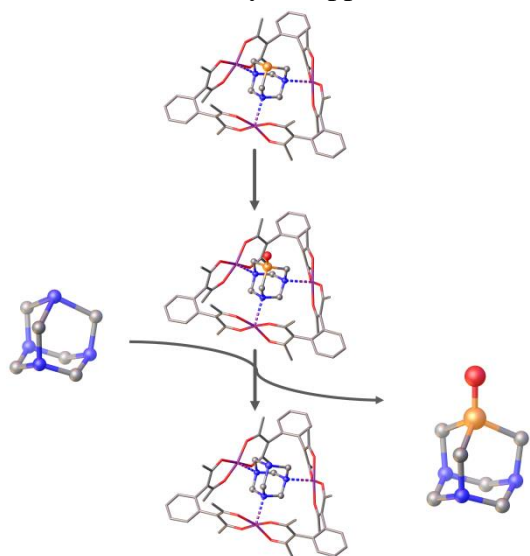
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Metallo-supramolecular architectures generated from metal centres and well designed polytopic ligands are an excellent bench test for supramolecular and self-organization concepts and a wide source of new functional materials. In particular, coordination driven discrete boxes and capsules have drawn increasing attention due to their hollow superstructure. Such architectures provide space confined cavities for a variety of applications including storing, sensing, and nanoreactors.



In this context, we studied the metallo-supramolecular triangle $[\text{Cu}(\text{o-L})_3]$ generated by self-assembly between Cu(II) ions and a bis-acetylacetonate ligand [1,2]. $[\text{Cu}(\text{o-L})_3]$ is a metallo-macrocyclic structure with a triangular cavity endowed with host-guest properties [3]. We show that this system can act both as nanoreactors for the oxidation of PTA (1,3,5-triaza-7-phosphaadamantane) under soft conditions and as nanovessels to access unstable conformers and guest degradation products [4]. The role of the solvent as oxidation trigger and its influence on the stability of the

metallo-supramolecular host is also discussed. These results are supported by a combination of FT-IR analysis, absorption spectroscopy and single crystal structural studies.

[1] M. Rancan et al., *Dalton Trans.* 42 (2013) 7534.

[2] M. Rancan et al., *Chem. Commun.* 48 (2012) 3115.

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[4] M. Rancan et al., *Chem. Commun.* 50 (2014) 13761.

OC7

From nonsymmetric BIANs to nonsymmetric DABs: towards efficient Pd-catalysts for functionalized polyolefin synthesis

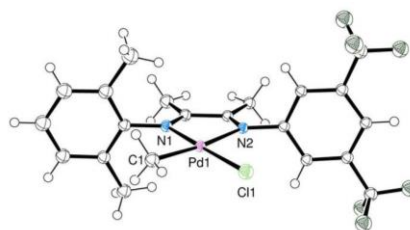
Barbara Milani, Vera Rosar, Tiziano Montini, Gabriele Balducci, Paolo Fornasiero

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The direct, homogeneously catalyzed, copolymerization of ethylene with polar vinyl monomers represents the most powerful and environment friendly tool for the synthesis of functionalized polyolefins, one of the main unsolved problems in the field of polymer synthesis.[1] Palladium complexes based on either α -diimines [2] or phosphine-sulfonate [3] ligands appear to be the most suitable candidates to generate efficient catalysts for this reaction.

Recently, we demonstrated that, in the ethylene/methyl acrylate (MA) copolymerization, Pd(II) catalysts having a nonsymmetric α -diimine featured by the acenaphthene skeleton (BIAN) had a productivity two times higher than that of the catalyst with the corresponding *ortho* substituted symmetric BIAN, leading to cooligomers with a higher content of MA.[4] In the past, Brookhart reported that moving from BIAN ligands to α -diimines with a 1,4-diaza-1,3-butadiene skeleton (DAB), an increase in the productivity of one order of magnitude was achieved.[2] Only one nonsymmetric DAB was reported up to now.[5] Thus, with the aim to validate the skeleton effect, we have now studied a new nonsymmetric DAB derivative analogous to the nonsymmetric BIAN.

The relevant organometallic, neutral and monocationic Pd(II) complexes were synthesized, characterized both in solid state (Figure) and in solution and applied as catalysts to the ethylene/MA copolymerization reaction.



- [1] K. Nozaki et al., *Chem. Rev.* 109 (2009) 5215.
- [2] M. Brookhart et al., *J. Am. Chem. Soc.* 118 (1995) 268.
- [3] K. Nozaki et al., *Acc. Chem. Res.* 46 (2013) 1438.
- [4] B. Milani et al., *ChemCatChem* 5 (2013) 1170.
- [5] R. J. Jordan et al., *Organometallics* 33 (2014) 7176.

OC8

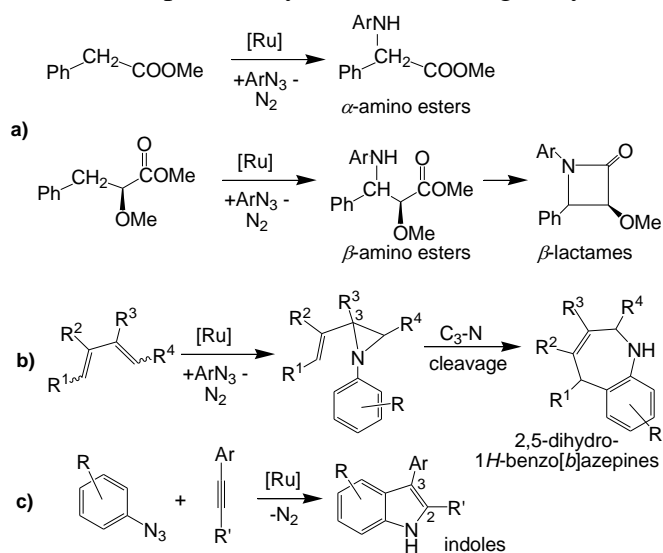
Synthesis of Biological Aminated Compounds Catalysed by Ruthenium Porphyrin Complexes

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The direct amination of hydrocarbons is a reaction of great synthetic interest due to the biological and pharmaceutical relevance of aza-derivatives. For several years we have studied the formation of C-N bonds using aryl azides (ArN₃) as nitrogen sources and metal porphyrins as catalysts.¹ Amongst all the catalysts, ruthenium porphyrins show a good catalytic activity in both the *inter-* and *intramolecular* transfer of a nitrene functionality “ArN” from ArN₃ into C-H bonds. The sustainability of the procedure is related to the high atom efficiency of azides which form benign N₂ as the only stoichiometric reaction side product.

Herein we report the synthesis of biologically interesting compounds such as: **a) α - and β -amino esters²** by



and β -amino esters² by amination of benzylic C-H bonds. The methodology was also effective in producing methyl L-3-phenyllactate derivatives in order to convert them into β -lactams; **b) benzoazepines³** by aza-[3,3]-Claisen rearrangement of *N*-aryl-2-vinylaziridines derived from the reaction of ArN₃ with dienes; **c) C3-functionalized indoles⁴** by an intermolecular reaction of ArN₃ with alkynes. Several indoles were synthesised

with yields up to 95%, high regioselectivity, without requiring the time consuming prefunctionalisation of reagents and the addition of oxidants and/or additives.

[1] a) D. Intriери, P. Zardi, A. Caselli, E. Gallo *Chem. Commun.* 50 (2014) 11440. b) S. Fantauzzi, A. Caselli, E. Gallo *Dalton Trans.* (2009) 5434.

[2] P. Zardi, A. Caselli, P. Macchi, F. Ferretti, E. Gallo *Organometallics* 33 (2014) 2210.

[3] a) C. Piangiolino, E. Gallo, A. Caselli, S. Fantauzzi, F. Ragaini S. Cenini *Eur. J. Org. Chem.* (2007) 743; b) S. Fantauzzi, E. Gallo, A. Caselli, C. Piangiolino, F. Ragaini, N. Re, S. Cenini *Chem. Eur. J.* 15 (2009) 1241.

[4] P. Zardi, A. Savoldelli, D. M. Carminati, A. Caselli, F. Ragaini, E. Gallo *ACS Catal.* 4 (2014) 3820.

OC9

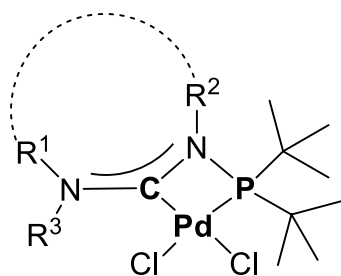
Palladium complexes with chelating N-Phosphanyl-Carbene Ligands: Synthesis and Catalysis

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N-phosphorylated azolyliidenes represent a novel class of N-heterocyclic carbenes (NHCPs) featuring a direct N-P bond between one of the heterocyclic nitrogens and an exocyclic phosphorus-containing group. Such compounds may serve as tunable bidentate ligands for transition metal complexes with a broad spectrum of potential applications. In the last few years, several original synthetic approaches to such compounds have been developed, and first examples of their complexes with transition metals have appeared in the literature.[1,2]



In the present contribution, we wish to report on our latest results concerning the synthesis, characterization and application of palladium(II) complexes, in which NHCPs behave as chelating ligands. Acyclic, N-phosphanyl diaminocarbenes have been also prepared for the first time and employed as chelating ligands towards palladium(II). Several complexes have been structurally characterized and their catalytic potential

has been preliminarily assessed in cross-coupling reactions, most notably in the Suzuki coupling of aryl chlorides, where these complexes display good activity but in some instances also a tendency to decompose under reaction conditions.

[1] a) A. P. Marchenko, H. N. Koidan, E. V. Zarudnitskii, A. N. Hurieva, A. A. Kirilchuk, A. A.; Yurchenko, A. Biffis, A. N. Kostyuk, *Organometallics* 31 (2012) 8257; b) A. P. Marchenko, H. N. Koidan, A. N. Hurieva, O. V. Gutov, A. N. Kostyuk, C. Tubaro, S. Lollo, A. Lanza, F. Nestola, A. Biffis, *Organometallics* 32 (2013) 718; c) A. Marchenko, H. Koidan, A. Hurieva, Y. Vlasenko, A. Kostyuk, C. Tubaro, A. Lenarda, A. Biffis, C. Graiff, *J. Organomet. Chem.* 771 (2014) 14.

[2] a) E. Kühnel, I. V. Shishkov, F. Rominger, T. Oeser, P. Hofmann, *Organometallics* 31 (2012) 8000; b) P. Nägele, U. Herrlich (né Blumbach), F. Rominger, P. Hofmann, *Organometallics* 32 (2013) 181; c) P. Ai, A. A. Danopoulos, P. Braunstein, K. Y. Monakhov, *Chem. Commun.* 50 (2014) 103; d) C. C. Brown, P. N. Plessow, F. Rominger, M. Limbach, P. Hofmann, *Organometallics* 33 (2014) 6754.

OC10

Integrin Targeting with Peptide Bioconjugated Nanocrystalline Heterostructures: a Theranostic Prospect

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$\alpha_v\beta_3$ integrin is an important tumor marker widely expressed on the surface of cancer and on tumor-associated endothelial cells^[1]. Colloidal inorganic nanocrystals (NCs) exhibit interesting electrical, optical, magnetic, and chemical size dependent properties. The combination of different nanostructured materials enable the access to novel nanomedical platforms for multimodal imaging, and simultaneous diagnosis and therapy, thus offering new and improved opportunities to overcome limitations associated with conventional diagnosis and therapy of cancer. Here, binary asymmetric binary nanocrystals (BNCs), composed of a semiconductor TiO₂ nanorod joined to a magnetic γ -Fe₂O₃ spherical domain, have been embedded in PEG modified phospholipid micelles^[2]. These systems, characterized by high photoactivity and magnetic properties, are particularly suited as phototherapy and hyperthermia agents as well as a magnetic probes in biological imaging. A designed peptide containing the RGD motif for targeting of $\alpha_v\beta_3$ ^[3] has been successfully conjugated with the BNCs. Each step of the work has been thoroughly monitored by means of optical, morphological and structural techniques. Cytotoxicity has been shown only for very high tested concentrations. Confocal microscopy investigation has highlighted the selectivity of the peptide-BNC conjugates for the $\alpha_v\beta_3$ integrin, and, consequently, a high potential of these nanomaterials for theranostic applications.

[1] R.O. Hynes, *Cell* 110 (2002) 673.

[2] N. Depalo et al., *Langmuir* 27 (2011) 6962.

[3] G. Scari, et al., *Bioconjugate Chem.* 23 (2012) 340.

OC11

Photoresponsive molecular devices and materials

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The application of a bottom-up approach to the design, preparation and characterization of chemical systems that span from molecular scale devices and machines to bulk materials is a stimulating challenge of nanoscience [1]. The interest on this kind of systems arises from their ability to perform a (useful) function in response to chemical and/or physical stimulation. In this context, the use of light stimulation has several advantages, primarily because photons can be used to supply energy to the system (i.e., write) as well as to gain information about its state (i.e., read) [2].

Here we will describe investigations undertaken in our laboratories, aimed at photoinducing and controlling functionalities in multicomponent (supramolecular) species that comprise light-sensitive elements [3]. Progress towards the construction of nanoconjugates composed of semiconductor quantum dots coated with functional organic ligands, designed to exhibit sensing and switching functionalities, will be presented [4]. We will also discuss recent results related to photoswitching of porosity in molecular crystals [5].

[1] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines – Concepts and Perspectives for the Nano World*, Wiley-VCH, Weinheim, 2008.

[2] P. Ceroni, A. Credi, M. Venturi, *Chem. Soc. Rev.* 43 (2014) 4068.

[3] M. Baroncini, S. Silvi, M. Venturi, A. Credi, *Angew. Chem. Int. Ed.* 51 (2012) 4223; V. Fasano, M. Baroncini, M. Moffa, D. Iandolo, A. Camposeo, A. Credi, D. Pisignano, *J. Am. Chem. Soc.* 136 (2014) 14245; G. Ragazzon, M. Baroncini, S. Silvi, M. Venturi, A. Credi, *Nature Nanotech.* 10 (2015) 70.

[4] M. Amelia, A. Lavie-Cambot, N. D. McClenaghan, A. Credi, *Chem. Commun.* 47 (2011) 325; C. Lincheneau et al., *J. Mater. Chem. C* 2 (2014) 2877; E. Margapoti, D. Gentili, M. Amelia, A. Credi, V. Morandi, M. Cavallini, *Nanoscale* 6 (2014) 741; T. Avellini, C. Lincheneau, M. La Rosa, A. Pertegás, H. J. Bolink, I. A. Wright, E. C. Constable, S. Silvi, A. Credi, *Chem. Commun.* 50 (2014) 11020.

[5] M. Baroncini, S. d’Agostino, G. Bergamini, P. Ceroni, A. Comotti, P. Sozzani, I. Bassanetti, F. Grepioni, T. M. Hernandez, S. Silvi, M. Venturi, A. Credi, *Nat. Chem.*, in press, DOI: 10.1038/nchem.2304.

OC12

Design to application: the development of tetrazolate-based luminescent metal complexes

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The preparation of new coordination compounds containing 5-aryl tetrazolate [R-CN₄]⁻ ligands and the study of their physical and chemical properties is the focus of our research program. In particular we have demonstrated how these synthetically versatile nitrogen-rich ligands can actually rule the luminescent output of the corresponding Ru(II), Ir(III), Re(I) and Pt(II) – based complexes. [1,2] The synthetic versatility of tetrazolate derivatives combined with the peculiar sensitivity to electrophiles that is displayed by the metal-coordinated tetrazolate group constitute the basis for the further development of their coordination chemistry and their applicative scenarios. Following a similar approach, we have prepared a new family of anionic Ir(III) tetrazolate complexes and new Re(I)-based species containing ditopic tetrazolate ligands. (Figure 1) The photophysical properties of the new molecules, with particular attention dedicated to their use as components for luminescent soft salts and to the study of their chemosensing abilities will be discussed.

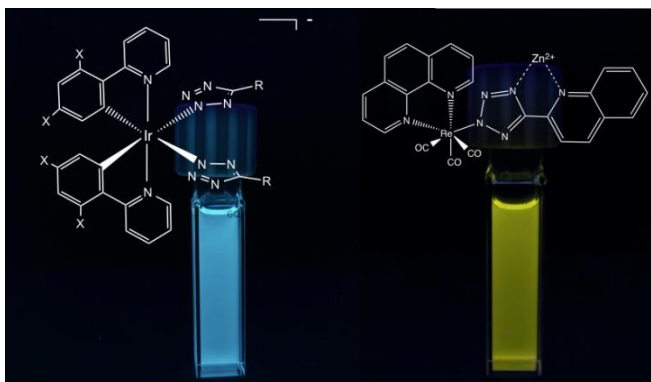


Figure 1. New anionic Ir(III) tetrazolates (left), Re(I) tetrazolate complexes (right)

[1] S. Stagni et al., *Inorganic Chemistry* 53 (2014) 229.

[2] S. Stagni et al., *Dalton Transactions* 44 (2015) 8379.

OC13

Synthesis and Characterization of New Ferrocene, Porphyrin and C₆₀ Triads, Connected by Triple Bonds

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Electron and energy transfer are important topics in the chemistry of biological and artificial systems and have been extensively studied over the past twenty years.¹ Photosynthesis in plants and bacteria is based on chemical reactions induced by the electron-transfer phenomena between natural tetrapyrrolic pigments, such as chlorophylls and related molecules, and quinones, both embedded in a protein matrix.² The entire process is not yet well understood and more information can be obtained by the use of synthetic models.³

During our studies on the possibility to use molecular wires to connect to the beta-pyrrole positions of the porphyrins one C₆₀ unit through the assembling of one or more triple bond, we found that it was very convenient and important to have a large delocalization of the π electrons between the donor and the acceptor moieties of the models.⁴ Recently we have reported the beta functionalization of H₂TPP by one or two ferrocene molecules in the 2 and 3 positions through ethynyl or phenylethynyl groups, applying a new approach of the Sonogashira reaction, never used before in the case of porphyrins.⁵ In this communication we report on the synthesis of new triads, useful as a model for investigating the electron-transfer processes, connecting ferrocene and C₆₀ to the 2,12 pyrrole positions of H₂TPP through ethynyl bonds. In Figures 1 the structure of triad **1** free base and its zinc complex is reported. We will also show the fluorescence spectra of the triads compared to the related reference compounds.

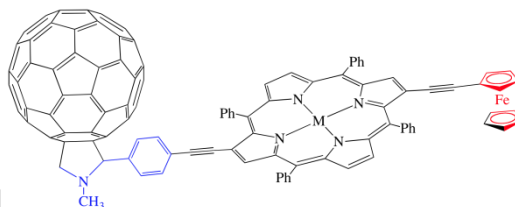


Figure 1: the structure of triad 1

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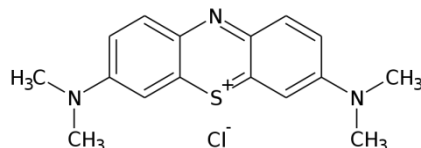
Structural investigations on the behavior of methylene blue towards transition chlorometallates

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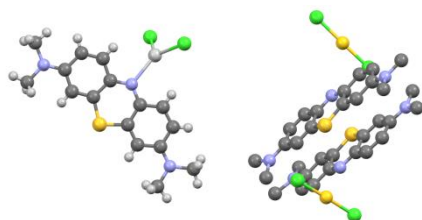
This study deals with the syntheses and the structural characterizations of new compounds formed by reaction of 3,7-bis(dimethylamino)phenothiazin-5-ium, also



known as methylene blue cation (MBC) with various chlorometallates, in particular of copper, gold, silver and mercury. The preparations of all these compounds have been carried out in the solid state, *via* grinding reactions between the starting reagent salts, i.e. MBC chloride

(sketched aside) and metal chlorides. The resulting powders have been characterized through X-ray powder diffraction, in order to check the reactions outcomes and to confirm the crystalline nature of the obtained products. All the products have been subsequently dissolved in adequate solvents and systematic crystallization trials have been carried out. Some of them gave crystals suitable for single crystal X-ray diffraction and their structures have been successfully solved.

Two different classes of structures have been observed. The first one contains a larger number of cases in which the only remarkable interaction between MBC and the inorganic anion is merely electrostatic, as observed in $[\text{MBC}]^+[\text{AuCl}_2]^-$ (Fig. 1, left). Depending on the geometry and the charge of the counter-anions and on the presence of solvent molecules, the MBC cations give rise to π - π stacking motives consisting either in infinite stacks or in discrete dimers scarcely interacting among them. In the second class of structures, MBC points its aromatic nitrogen directly on the metal center performing a coordinative interaction with the inorganic anion. This particular role of MBC is clearly exhibited with the dichloroargentate anion in



the new complex shown in Fig. 1 (right). To our knowledge, the coordinative behavior of MBC has never been reported and the electronic nature of the N-metal bond is under spectroscopic and computational investigations.

Fig. 1. Molecular structure in the solid state of $[\text{MBC}]^+[\text{AuCl}_2]^-$ (left) and $[\text{MBC-AgCl}_2]$ (right)

OC15

Gas-phase reactivity and spectroscopy of ionic intermediates involved in NO binding and delivery

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Nitric oxide (NO) is a versatile short-lived molecule involved in a wide range of physiological processes, including signal transduction, vasodilation, and immune response. The binding of NO is primarily directed to the metal center of heme enzymes. However, it is now recognized that S-nitrosation of cysteine residues has emerged as a ubiquitous, reversible modification, responsible for the most part of NO bioactivity. In order to explore the intrinsic bonding and physicochemical properties of heme nitrosyl complexes and low-molecular weight S-nitrosothiols, we have explored their reactivity and structural features by means of ion-molecule reactions and action spectroscopy in the gas phase. To this end, the kinetic and thermodynamic parameters of the NO reaction with iron(II) and iron(III) heme complexes have been measured by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry coupled with electrospray ionization (ESI).[1, 2] Besides, their N-O stretching vibrations, considered a sensitive probe of the heme-NO interaction, have been assayed by IR Multiple Photon Dissociation (IRMPD) in the 900-2000 fingerprint range, so providing a thorough description of the sampled five coordinate iron nitrosyl complexes.[2, 3] Amino acids and peptides altered by post-translational S-nitrosation, including S-nitrosocysteine, and S-nitrosoglutathione have been also examined by IRMPD spectroscopy in both the mid-IR (900-2000 cm⁻¹) and N-H/O-H stretching (2800-3700 cm⁻¹) ranges. The observed $\nu(\text{NO})$ signatures are revealed by their sensitivity to ¹⁵N isotope labeling, by comparison with the IRMPD spectra of the native thiols, and by the interpretation of the IRMPD spectra aided by high-level theoretical calculations, providing a diagnostic probe for the S-nitrosation in natural peptides.[4, 5]

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OC16

***In situ* study on highly performing graphene quantum dots-MoS_x nanohybrids for the hydrogen evolution reaction (HER)**

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The use of hydrogen as energy carrier in fuel cells (FCs) is one of the most promising energetic policies for a rapid transition from fossil to more sustainable energy sources. In this context, there is a renewed interest in the development of efficient and non-noble metal HER catalysts [1]. MoS_x derived nanomaterials have

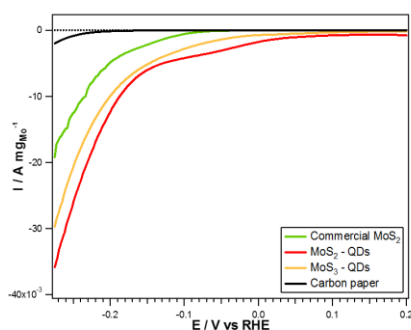


Figure 1. Polarization curves in 0.1M HClO₄ for the GQDs-MoS_x nanohybrids and the commercial MoS₂ (Aldrich) catalyst obtained at room temperature and 5 mV s⁻¹.

been shown as promising HER catalysts [2]. Nevertheless, their electrochemical activity is still under debate in the scientific community, since it is not yet known if the high activities reached are connected to the fully stoichiometric MoS₂, MoS₃ or to the *in situ* formation (under cathodic conditions) of sub-stoichiometric MoS_x species [3]. Thus, *in situ* experiments under operating conditions are essential to enable investigation on the cathodic-triggered formation of MoS_x species.

In this work, we have prepared graphene quantum dots (nanometric graphene sheets, GQDs)-MoS_x nanohybrids with different MoS_x stoichiometries (x=2,3) as electrocatalyst for HER. Combined electrochemical and photoemission measurements, as well as *in operando* X-ray absorption spectroscopy, have been used to determine the MoS_x species involved in the HER. Figure 1 shows that the GQDs-MoS_x nanohybrids are more active than the commercial MoS₂ (Aldrich) catalyst. On the other hand, the *in situ* measurements have evidenced that MoS₃ is not stable under HER conditions and that the terminal MoS₃ species are reduced to MoS₂, which is the real active phase. In addition, the GQDs-MoS₂ nanohybrid resulted to be very stable even after an accelerating ageing treatment.

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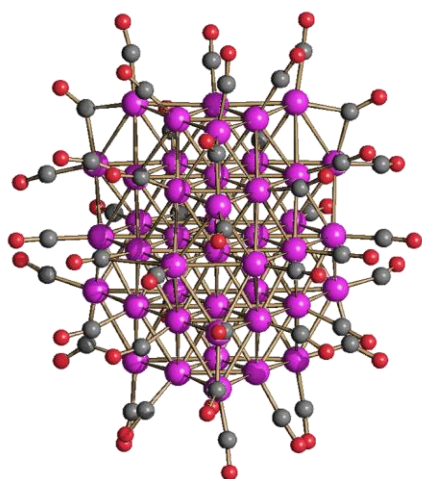
OC17

New Platinum Carbonyl Nanoclusters

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Despite the infrared evidence of the existence of dozens of compounds, the list of structurally characterized high nuclearity tridimensional platinum carbonyl clusters is rather limited [1]. Thermal degradation is the most useful route for their synthesis. Indeed, it is known that $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 2-10$) Chini's clusters begin



to lose carbon monoxide at *ca.* 70 °C leading to a formation of new M-M bonds. As a consequence, the thermal treatment of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 2-6$) in mild conditions (refluxing in organic solvents) has been exploited for synthesis of globular platinum nanoclusters, *i.e.*, $[\text{Pt}_{15}(\text{CO})_{19}]^{4-}$ [2], $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$, $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$ and $[\text{Pt}_{26}(\text{CO})_{32}]^{2-}$ [3]. Differently, in the case of $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$, the only other example of completely characterized platinum cluster, the compound is obtained by oxidation of $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$.

Herein, our recent results in the chemistry of platinum clusters are described. The reinvestigation of the thermal degradation of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 2-6$) oligomers led to the isolation of new species, *i.e.*, $[\text{Pt}_{33}(\text{CO})_{38}]^{2-}$ and $[\text{Pt}_{44}(\text{CO})_{45}]^{2-}$ (see figure). The former compound displays a defective *ccp* structure resembling to $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ that may be viewed as a model for metal surfaces.

Finally, the oxidation of $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ by stepwise addition of $\text{HBF}_4 \cdot \text{O}(\text{CH}_2\text{CH}_3)$ results in the formation of $[\text{Pt}_{36}(\text{CO})_{44}]^{2-}$ and $[\text{Pt}_{40}(\text{CO})_{40}]^{2-}$ as intermediated compounds. In the field of platinum clusters, the later compound represents a rare case of high-nuclearity cluster possessing a *bbc* structure.

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OC18

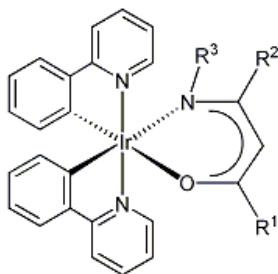
Novel β -enaminoketonate complexes of Iridium(III): synthesis and characterization

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Development of luminescent metal complexes represents an important challenge in the applications in many field, including catalysis, optoelectronics and biological imaging. Iridium(III) complexes are emerging as potentially valuable compounds since their emission is completely tunable via ligand modifications [1]. Many luminescent Ir(III) complexes incorporating cyclometalating (C[^]N) ligands exhibit excellent photophysical properties [2]. β -Enaminoketones represent a very versatile class of compounds nowadays reported to coordinate a significant number of metal ions. Moreover, it has been reported that suitable structural modification of β -enaminoketones can induce and control mesomorphism in the corresponding metal complexes [3-4]. Remarkably, no examples of Ir(III) complexes containing β -enaminoketonate ligand have been reported so far.

Herein, we report on the synthesis and characterization of the first examples of heteroleptic Ir(III) complexes containing 2-phenylpyridine as cyclometalating ligand and β -enaminoketonate as ancillary ligand [(ppy)₂Ir(ek)] (ppy = 2-phenylpyridine, ek = β -enaminoketonate).



Ir(III) complexes reported in this communication have been characterized by means of spectroscopic techniques and X-ray diffraction.

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OC19

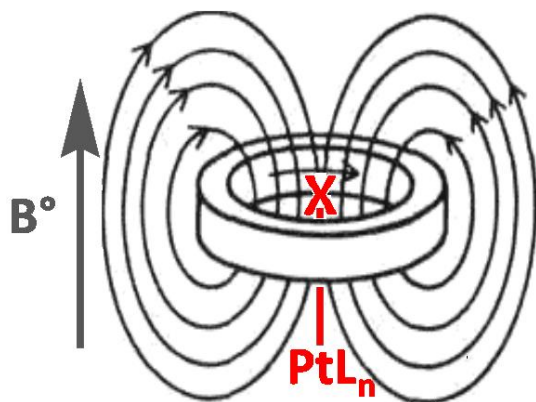
¹⁹⁵Pt NMR chemical shift as a function of the coordinated halidos ionic radii overall sum

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By comparison of the complete series of $[\text{PtX}_2(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{Me}_2\text{phen} = 2,9\text{-dimethyl-1,10-phenanthroline}$) X-ray structures we could observe a very low variability of the bond lengths and angles, in the trigonal equatorial plane, on varying the axial X^- ligands.[1] Therefore, the two subsystems constituted by the metal bonds with axial (X-Pt-X) and equatorial ligands ($\text{Me}_2\text{phen-Pt-}\eta^2\text{-ethene}$) could be described as independents and not interacting.



This means that the electric charge donated to the metal, by the axial ligands, cannot substantially modify the bonds of the metal with the ligands in the trigonal equatorial plane. For these complexes the NMR chemical shifts variations (^1H , ^{13}C , ^{15}N and ^{195}Pt) as a function of the ionic radius of axial halidos were also studied. The observed trend of NMR data, strongly suggests the existence of electric pseudo-ring currents circulating around the Pt-X

axes and modulated by the ionic radii of the coordinated halidos, see Figure. We could fully confirm this hypothesis by extending to other Pt(II) and Pt(IV) complexes the same analysis. Inverse linear relations between observed ^{195}Pt NMR signals and the overall sum of coordinated halidos ionic radii was found in all cases. Similar linear reductions of the ^{195}Pt NMR frequencies are generally observed on increasing the coordinated halidos ionic radii sum even in mixed halido species. This confirms again that each halido may acts as an independent conducting ring, which can shield the ^{195}Pt NMR signals proportionally to his ionic radius.

[1] M. Benedetti et al., *Inorg. Chim. Acta* 428 (2015) 8.

OC20

Interaction of cisplatin with 5'-dGMP: a combined IRMPD and theoretical study

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Cisplatin has been one of the most widely prescribed drugs for many cancer diseases. Although its mechanism of action has not yet been fully elucidated, it is generally accepted that the therapeutic activity of cisplatin is achieved by binding with DNA to form crosslinks as major lesions. With this contribution, we continue the experimental structural characterization of ionic complexes from cisplatin and DNA components in the gas phase by combining IRMPD (Infrared Multiple Photon Dissociation) spectroscopy of complexes generated in a mass spectrometer by electrospray ionization (ESI), to theoretical DFT calculations started with the characterization of *cis*-[PtCl(NH₃)₂(H₂O)]⁺,¹ and continuing with the study the *cis*-[PtCl(NH₃)₂(G)]⁺ and *cis*-[PtCl(NH₃)₂(A)]⁺ complexes (where G is guanine and A is adenine).² Proceeding with increasing complexity of the ligand, we presently report a study of the interaction of cisplatin with 2'-deoxyguanosine-5'-monophosphate (5'-dGMP). Moving from the simple nucleobase to the mononucleotide, the possible binding sites of cisplatin increase. In addition to the N7 position of guanine, platinum may interact with the oxygen(s) of the phosphate group and with the hydroxyl group of the deoxyribose moiety. Two ions were presently considered for their structural characterization by IRMPD spectroscopy, namely the *cis*-[Pt(NH₃)₂(5'-dGMP-H)]⁺ and *cis*-[PtCl(NH₃)₂(5'-dGMP)]⁺ complexes. IRMPD spectroscopy has been performed in two spectral regions, namely 700-1900 cm⁻¹ and 2800-3800 cm⁻¹. For structural assignment, experimental IRMPD spectra were compared to IR spectra computed at the B3LYP/LACV3P/6-311G** level of theory. In agreement with computational results, the vibrational spectroscopic characterization of the *cis*-[Pt(NH₃)₂(5'-dGMP-H)]⁺ ion points to macrochelate species resulting from the simultaneous interaction of the metal with both the N7 atom of the guanine residue and an O atom of the phosphate group, structures that bear features in common with those characterized in solution by NMR spectroscopy. Concerning the *cis*-[PtCl(NH₃)₂(5'-dGMP)]⁺ ion, our study points to a monodentate complex involving exclusively the N7 position of guanine, as observed in solution.

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OC21

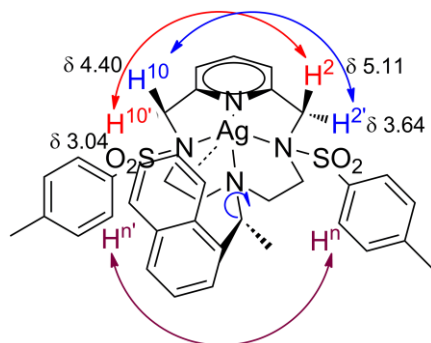
Well defined [Silver(I)(Pyridine-Containing Ligand)] Complexes

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Nitrogen containing macrocyclic molecules are naturally occurring species that play a vital role in biological system, such as porphyrins, corrins and chlorins. In past years, our attention turned to the development of synthetic pathways that allow to obtain a new class of tetraaza macrocyclic ligands containing pyridine in few synthetic steps, in good yield, and starting from economic and commercially available starting materials.¹ The copper(I) complexes of these Pc-L* ligands have been successfully employed as catalyst in the Henry reaction² and in the enantioselective cyclopropanation of alkenes.³ More recently, the silver(I) complexes have demonstrated to be active catalysts for some domino⁴ and multicomponent reactions.⁵ Here we report on new chiral [Ag(I)(Pc-L*)] complexes that were synthesized and fully characterized, including structures of some species determined by X-ray



diffraction on single crystals. They show a rich coordination chemistry, demonstrating both the σ -philic (alcohol and nitrile coordination) and the π -philic (alkyne coordination) nature of silver. The η^2 coordination mode of the naphthyl pendant arm of the ligands on silver has been observed in solution by NMR experiments. 2D-NMR spectroscopy revealed the presence of positive cross peaks due to rotational processes and the rate of rotation was measured by using 2D Exchange Spectroscopy (EXSY).

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[4] M. Dell'Acqua, B. Castano, C. Cecchini, T. Pedrazzini, V. Pirovano, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* 79 (2014) 3494.

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OC22

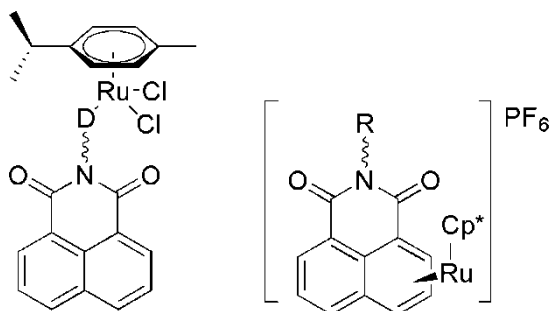
A journey into the coordination properties of naphthalimides toward the (p-cymene)Ru and Cp*Ru fragments

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Naphthalimides (NI, see figure) are intercalating cytotoxic agents which have been extensively evaluated for antitumor activity, with two examples (mitonafide and amonafide) entering clinical trials [1]. The facile functionalization of the imide nitrogen with a number of different R groups allows the construction of large libraries of ligands for the synthesis of coordination or organometallic compounds. Arene-Ru complexes are nowadays extensively investigated as potential anticancer compounds, with a number of reviews recently appeared [2][3]. In this communication the synthesis of a series of half-sandwich as well as sandwich complexes containing tailored NI ligands will be reported. The solution and solid state characterization of the isolated compounds will be discussed, based on FTIR, NMR, ESI-MS data as well as single crystal X-ray structures and DFT calculations. Finally, the characterization of a dinuclear (arene)Ru metallacage compound containing a naphthalene-di-imide ligand (NDI) will be reported. The titled compounds result attractive as possible anticancer agent since they combine the intercalating properties of the NI or NDI scaffold with the unique bio-organometallic properties of the (arene)Ru or Cp*Ru moieties. Some preliminary cytotoxicity data against several tumor cell lines will be presented.



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[3] A.A. Nazarov et al., *J. Organomet. Chem.* 751 (2014) 251.

OC23

Catalytic activity of green metal nanoparticles

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The hydrogenation reactions (reduction, isomerization, hydrodeoxygenation, etc.) have a crucial role in the preparation of required products for biorefinery and for the polymer and pharmaceutical industries, which are obtained from highly oxygenated biomasses by lowering their O/H ratio. Low molecular weight saturated alcohols (e.g., butyl alcohol, 1-propanol) are currently studied in order to replace, at least in part, traditional fuels, for their good miscibility with hydrocarbons, high energy content and low vapor pressure. [1]

Hydrogenations are normally performed using hydrogen gas and metal catalysts, such as Raney Nickel or Palladium, Rhodium or Platinum metals. In recent years different metal nanoparticles (NPs) are reported as active catalysts for hydrogenation reactions of unsaturated hydrocarbons or allyl alcohols.

We prepared Pd and Pt NPs nanoparticles starting from the corresponding metal ions and different lignosulphonates in water at 80 °C in aerated conditions [2]; NPs were fully characterized (TEM, Fig. 1) and tested as catalysts for unsaturated alcohols hydrogenation in water at room temperature and pressure. NPs were active with sharp differences in conversions and selectivities.

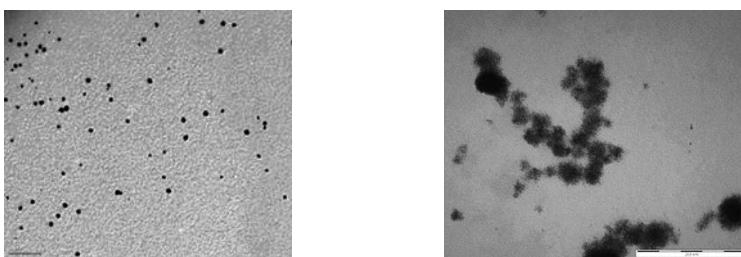


Fig 1. TEM images of Pd NPs (left, scale bar= 100 nm) and Pt NPs (right, scale bar= 200 nm).

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OC24

Band gap engineering in semiconducting and insulating oxides

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Among the semiconductors employed in photocatalytic reactions, transition metal oxides play a paramount role due to their qualities in term of stability in various media often accompanied by low or reasonable cost. The search for innovative materials in these field is oriented to select systems having a suitable electronic structure capable of harvesting solar light (which means essentially visible light) and excellent potential to perform the desired redox process. This is practically impossible to be found in a unique system. Solid materials with large band gap values correspond, in principle, to good reduction and oxidative potentials but inevitably, to perform the charge separation, need high energy photons (UV light, scarcely present in solar irradiation at the earth surface). On the other hand semiconductors with smaller band gap value, compatible with visible light absorption, may have unsatisfactory potentials for both reduction and oxidation.

A possibility to overcome this drawback consists in modifying a semiconductor with relatively large band gap in order to make possible the absorption of visible light. In the present contribution we will illustrate some examples of “band-gap engineering” in the case of oxides with energy gap, $E_g > 3$ eV, namely titanium dioxide, zirconium dioxide and tin oxide. Particular preparation techniques are used to obtain solids doped with non metals or with transition metal ions and exhibiting novel optical and electronic properties. The examples of three MeO_2 oxides (Me = Ti, Sn, Zr) doped either with non metals, (N), metal ions or lanthanides will be illustrated.

Doped MeO_2 oxides show original opto-electronic properties and are of interest not only in the fields of photochemistry and photocatalysis but have been also proposed to obtain diluted magnetic semiconductors of potential interest for spintronics.

[1] C. Gionco et al. *J. Phys. Chem. Letters* 5 (2014) 447.

[2] C. Gionco et al. *Chem. Mat.* 25 (2013) 2243.

OC25

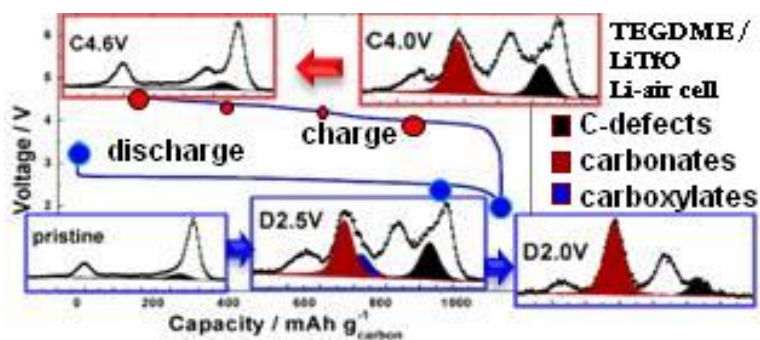
Surface reactivity of carbonaceous cathodes in Li-O₂ batteries: an *ex-situ* XPS investigation

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Li-O₂ batteries are currently one of the most advanced and challenging electrochemical systems with the potential to largely overcome the performances of any existing technology for energy storage and conversion.[1]



Here, we illustrate the evolution of the morphology and composition of a carbonaceous cathode in the first discharge/charge in a Li-O₂ cell with an ether-based electrolyte by means of X-ray Photoemission Spectroscopy.[2] Experiments were carried out *ex situ* on electrodes recuperated from electrochemical cells stopped at various stages of galvanostatic discharge and charge. The formation of lithium oxides is monitored and the reactions occurring at the triple O₂/carbon/electrolyte interphase are envisaged as a function of different Li salts used.[3] Furthermore, degradation products are identified and associated to the global performance of the cell. Overall, a deeper understanding of the hidden chemistry at the surface of the cathode has been achieved.

[1] M. Armand et al., *Nature* 451 (2008) 652.

[2] A.G. Marrani et al., *submitted* (2015).

[3] E. Nasybulin et al., *J. Phys. Chem. C* 117 (2013) 2635.

OC26

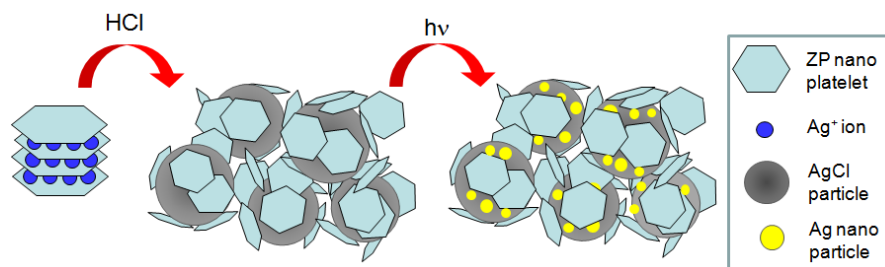
Zirconium phosphate/silver chloride composites: synergistic effects for the photocatalytic degradation of organic dye pollutants

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A new class of composite photocatalysts, based on α -zirconium phosphate and AgCl (ZP/ x AgCl, where x =AgCl/ZP molar ratio = 0.28, 0.56, 1.16), was prepared by reaction of hydrochloric acid with silver(I) exchanged α -layered zirconium phosphate [1]. The ZP/ x AgCl composites were characterized by X-ray diffraction analysis, scanning electron microscopy/energy dispersive X-ray spectroscopy, UV-Vis diffuse reflectance spectroscopy.



The photocatalytic properties of the ZP/ x AgCl composites, were investigated in the degradation of Rhodamine B. The ZP/1.16AgCl turned out to be the best photocatalyst, providing a complete chromophore structure cleavage in 15 minutes; differently, in the presence of pure AgCl, the concentration of the chromophore species after 30 minutes was about half of the initial one. Moreover, the catalytic activity of ZP/1.16AgCl was evaluated for three consecutive catalytic tests, and an almost complete chromophore structure cleavage was achieved in 10 minutes during the third run.

[1] M. Pica, M. Nocchetti, B. Ridolfi, A. Donnadio, F. Costantino, P. L. Gentili, M. Casciola, *Journal of Materials Chemistry A* 3 (2015) 5525.

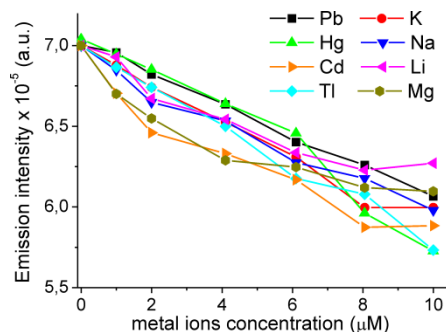
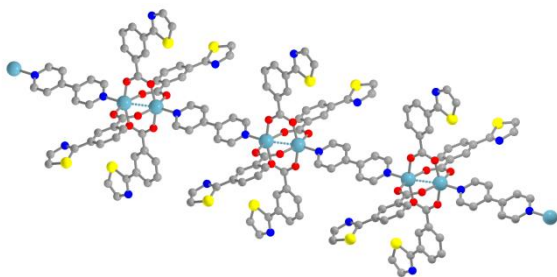
OC27

Zinc coordination polymers containing the isomeric forms of thiazolyl benzoic acid: synthesis and applications in ion sensing

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Thiazoles are intriguing heterocycles for the construction of Metal-Organic Frameworks (MOFs) and Coordination Polymers (CPs) of assorted dimensionality.[1] The presence of multiple basic sites of both *hard* (N) and *soft* (S) nature for coordination to metal ions and their intrinsic luminescent features are suitable for exploitation in the field of luminescent ion sensing. Several CPs containing Zn(II) as a metallic node have been prepared starting from zinc acetate hydrate and *m*-(2-thiazolyl)benzoic acid, *p*-(2-thiazolyl)benzoic acid and *p*-(5-thiazolyl)benzoic acid. Their synthesis, structure and solid state characterization will be presented, along with applications as luminescent sensors for polluting metal ions (Hg^{2+} , Cd^{2+} , Pb^{2+} , Tl^+) in aqueous solutions.[2]



[1] A. Rossin and G. Giambastiani, *CrystEngComm* 17 (2015) 218.

[2] S. Staderini, G. Tuci, M. d'Angelantonio, F. Manoli, I. Manet, G. Giambastiani, M. Peruzzini and A. Rossin, *manuscript submitted*.

OC28

Reaction of Copper(II) Chloroacetate with Pyrazole. Synthesis of a 1D Coordination Polymer and Unexpected Dehydrochlorination Reaction

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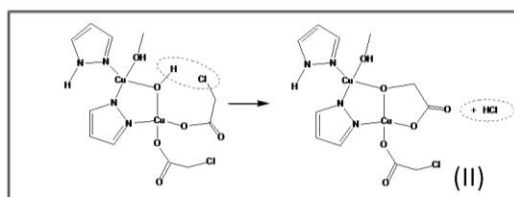
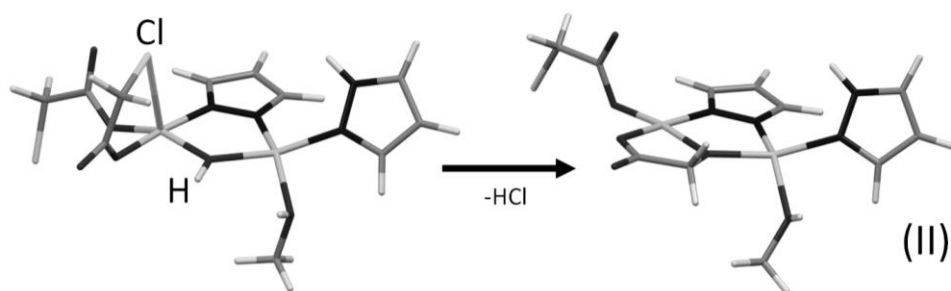
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The reactions of copper(II) chloroacetate with pyrazole (Hpz), carried out in methanol, yielded mainly the mononuclear $[\text{Cu}(\text{RCOO})_2(\text{Hpz})_2]$ compound (**I**), which self-assemble generating a 1D coordination polymer. Moreover, the isolation of a tetranuclear $[\{\text{Cu}_2(\mu\text{-pz})(\mu\text{-OCH}_2\text{COO})(\text{Hpz})(\text{MeOH})\}_2(\mu\text{-ClCH}_2\text{COO})_2]$ (**II**) and a hexanuclear $[\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{Hpz})_2\}_2(\mu\text{-ClCH}_2\text{COO})_2](\text{Cl})_2$ (**III**) derivative evidenced the occurrence of a previously unreported, peculiar, dehydrochlorination reaction. Theoretical calculations based on density functional theory (DFT) including solvation effects (COSMO) indicate a possible pathway for the obtainment of **II**. Interestingly, besides the energy minimum corresponding to the tetranuclear compound, a further relative energy minimum is found for a species, which can be considered a possible intermediate.



OC29

Crystal engineering of non-centrosymmetric systems

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Crystalline organometallic compound lacking an inversion center were synthesized starting from acentric reagents by means of two different approaches: use of asymmetric metal center and synthesis with asymmetric ligand.

The first methodology was explored by employing a mixed halide of mercury (II), HgBrI, that crystallize in Cmc2(1) space group [1], and three pyridine-based ligands. This complex was prepared with a new solid state reaction. The second approach was developed by employing the 2-(2'-pyridyl)-1,8-naphthyridine (pyNP), (whose non-centrosymmetric crystalline structure (P2(1) space group) was first determined by us) and several d¹⁰ metals (Hg(II), Pb(II), Ag(I)).

A series of complexes were synthesized and their structure was characterized by means of single crystal X-ray diffraction, Raman, IR and electronic spectroscopy. Complexes with HgBrI and aromatic heterocyclic ligands usually give non-centrosymmetric crystalline structure while those with pyNP tend to be centrosymmetric. The obtained results seem to suggest that the crystalline packing was mainly influenced by the metal center than the ligand. These systems are very interesting materials, because of the intrinsic NLO properties that could be employed in optical and optoelectronic application. [2]

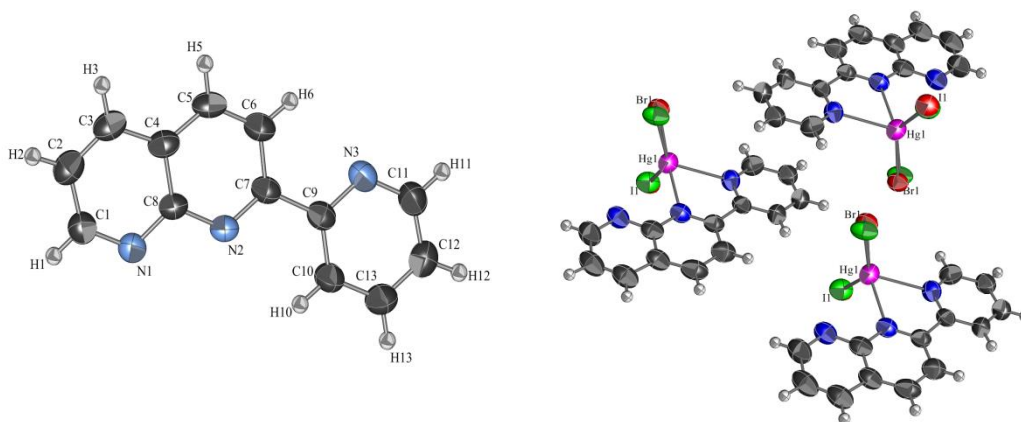


Figure 1 Examples of crystal structures: on the left pyNP, on the right (Hg(pyNP)BrI)

[1] Wu Q., Li Y., Chen H. et al., *Inorg. Chem. Comm.* 34 (2013) 1.

[2] Long N. J., *Angew. Chem. Int. Ed. Engl.* 34 (1995) 21.

OC30

Zirconium Carboxy-aminophosphonate Nanosheets as Versatile Support for Metallic Nanoparticles

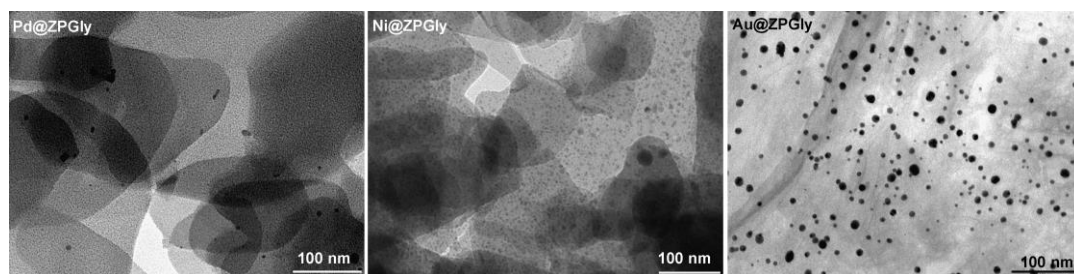
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Luigi Vaccaro²

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The possibility to obtain materials as single-layer nanosheets is an ambitious and highly desirable goal because monolayers of few nanometer thick possess outstanding properties if compared to crystalline precursors. The exfoliated compounds lead to a considerable increase of the surface area which is a crucial point in heterogeneous catalysis [1]. Besides, immobilization and stabilization of metallic nanoparticles (M NPs) onto solid supports is currently a topic of high interest in heterogeneous catalysis [2]. Adequate supports could inhibit particle migration, avoid the aggregation in larger clusters and enhance the catalytic efficiency allowing a homogenous distribution of the catalytic sites.

In this context a quick and easy procedure to obtain stable nanosheets of a crystalline layered zirconium phosphate–phosphonate [3], built from the N,N-bis(phosphonomethyl)glycine, (ZPGly) has been performed by treatment with propylamine solution. The exposed aminocarboxylic and phosphonic groups on nanosheets surface are able to exchange protons with metal ions such as Ni(II), Pd(II), Au(III) that upon reduction generate small M NPs (see TEM images).



The resulting Pd@ZPGly sample was fully characterized and representatively tested in the Suzuki-Miyaura coupling. The novel catalytic system proved its efficiency as it was reused for several cycles with unchanged efficiency and showing a low Pd leaching.

[1] J. N. Coleman et al. *Science* 331 (2011) 568.

[2] A. Balanta et al. *Chem. Soc. Rev.* 40 (2011) 4973.

[3] A. Donnadio et al. *Inorg. Chem.* 53 (2014) 13220.

OC31

Nitrobenzene Reduction with AuNPs supported onto a polymeric matrix

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Gold Nanoparticles (AuNPs) are a powerful and versatile catalyst suitable in a variety of oxidation and reduction reactions under sustainable conditions [1]. E.g. aerobic oxidation of alcohols and cross coupling reactions of alcohols to esters, amide, imine have been widely and successfully explored [2]. On the other side the reduction of nitroarenes to anilines using NaBH₄, H₂, silanes, formic acid, CO/H₂O is a benchmark reaction for testing the catalytic performances of AuNPs in reduction reactions [3].

In this scenario, AuNPs embedded in a polymeric matrix consisting of syndiotactic polystyrene-co-cis-1,4-polybutadiene (AuNPs-sPSB) were found extremely active in oxidation catalysis [4]; thus herein we report on the use of the AuNPs-sPSB catalyst in the reduction of nitrobenzene to aniline using NaBH₄. The polymorphic behaviour of the host polymer matrix has been studied in order to optimize the catalyst performances. The nanoporous crystalline forms, namely δ and ϵ , of the sPSB matrix allowed a total conversion of nitrobenzene in 40 min at room temperature, with 100% selectivity in aniline. The not permeable β crystalline form produced a less reactive and selective catalyst; actually azobenzene and azoxybenzene were detected as intermediates compounds providing information on the cascade of reactions and the global reaction mechanism.

The catalyst is very stable under the reaction conditions and reusable for at least three times without any loss of catalytic activity.

[1] M. Stratakis, H. Garcia, *Chem. Rev.* 112 (2012). 4469.

[2] A. Corma, H. Garcia, *Chem. Soc. Rev.* 37 (2008) 2096.

[3] S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G.S. Armatas, I. N. Lykakis*, *ACS Catal.* 4 (2014) 3504; X. Liu, S. Ye, H.-Q. Li, Y.-M. Liu, Y. Cao, K.-N. Fan, *Catal. Sci. Technol.* 3 (2013) 3200.

[4] A. Buonerba, C. Cuomo, S. Ortega Sánchez, P. Canton, A.Grassi, *Chem. Eur. J.* 18 (2012) 709; A. Buonerba, A. Noschese, A. Grassi, *Chem. Eur. J.* 20 (2014) 5478.

OC32

Capture of heavy metals by thiol functionalized magnetic nanoparticles using a system of permanent magnets

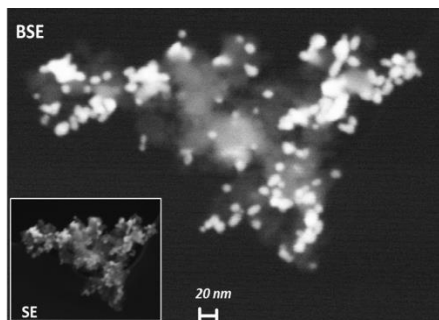
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In recent years, magnetic nanomaterials have attracted considerable attention because of their unique properties that make them very useful in different fields. Below certain critical dimensions, depending on the material nature, magnetic materials become superparamagnetic. In this case the nanomaterials exhibit no magnetic properties upon removal of the external field thus reducing the risk of particle aggregation [1].

In this work the synthesis of magnetite (Fe₃O₄) NPs and their functionalization by means of a silane derivative (3-mercaptopropyl)trimethoxysilane (MPTMS) through a silanization reaction has been investigated. Moreover, considering that magnetic nanoparticles are extensively studied as nano-adsorbent materials for heavy metals removal [2], the experimental results of Pb(II) ions and gold NPs capture by MPTMS functionalized NPs will be shown and discussed.



All the synthetic steps have been morphological and physical characterized by means of FE-SEM microscopy with EDX analysis, IR spectroscopy and AC magnetic susceptibility.

These magnetic nanoparticles carrying the target metals could be easily separated from the aqueous solution by applying a magnetic field provided by commercial NdFeB permanent magnets. The capture configuration has been optimized to maximize the MNPs collection.

The quantity of the heavy metal collected as a function of time has been measured through elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES).

[1] S. P. Gubin, *Magnetic Nanoparticles*, Wiley-VCH, Weinheim 2009.

[2] J. Gómez-Pastora et al., *Chemical Engineering Journal* 256 (2014) 187.

OC33

Functionalized gold nanoparticles for drug delivery: Au3MPS@Dexamethasone as case of study

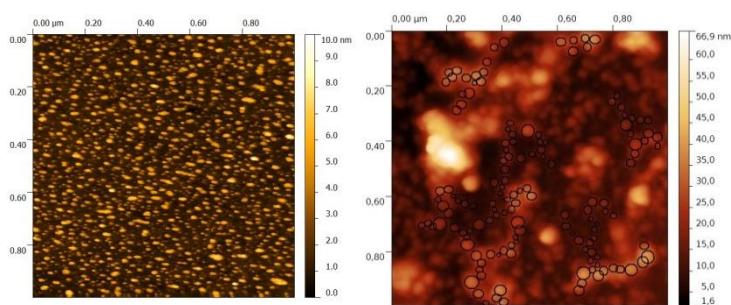
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Gold nanoparticles (AuNPs) are being applied for use as imaging/diagnostic tools, drug and gene delivery, photothermal therapy, sensors, and biotechnologies.[1-3] Their wide success is due to their unique chemical and physical properties, biocompatibility, and well-established strategies for surface modification.[3,4] In this framework we report a depth investigation about drug delivery system based on functionalized AuNPs.[5,6] The AuNPs (diameter 7-10 nm), synthesized using a hydrophilic capping agent, and characterized by means of several techniques, (Uv-visible, FTIR, XPS, DLS, FESEM, AFM) were used as carrier for dexamethasone (DXM). After optimization studies to improve the loading (loading efficiency 80%) and to have a controlled release (in the time range 1-10 days), these drug delivery system was tested in vitro, using HeLa cells. The performed cytotoxicity tests confirm the biocompatibility of the drug delivery conjugate and open new exciting perspectives in the field of “in vivo studies”.



In figure the AFM image of AuNPs and AuNPs @ DXM.

- [1] I. Fratoddi, et al., *Toxicology Research* (in press 2015 DOI: 10.1039/C4TX00168K).
- [2] I. Fratoddi, et al., *Sensors and Actuators B* (2015 DOI: 10.1016/j.snb.2015.05.107).
- [3] I. Venditti, et al.; *Colloids and Surfaces B: Biointerfaces* 131 (2015) 93.
- [4] R.P. Kurta, et al., *Phys Chem Chem Phys* 17 (2015) 7404.
- [5] I. Venditti, et al., *J. Colloid Interf. Sci.*, 418 (2014) 52.
- [6] C. Cametti et al., *Langmuir* 27 (2011) 7084.

OC34

Synthesis, Crystal Structure, and Proton Conductivity of 1D, 2D and 3D Zirconium Phosphonates Based on Glyphosate and Glyphosine

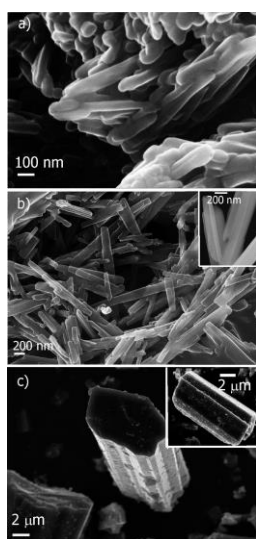
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Three zirconium phosphonate derivatives of glyphosate and glyphosine were synthesized, and their structures were solved ab initio from powder and single-crystal X-ray diffraction data [1].

These structures were not observed before and confirmed again the high structural versatility of the Zr aminomethylenephosphonate family. While the glyphosate was found to form an 1D ribbon-type structure consisting of the packing of hybrid inorganic chains (a), the glyphosine building block was found to form two different nonpolymorphic structures (2D (b) and 3D (c)) depending on small changes in the synthesis conditions, in particular, the HF concentration.



The different dimensionality and hydration capabilities of the three compounds were in agreement with their different morphology and the trends observed for their proton conductivity as a function of temperature. In particular, the 1D compound can incorporate two water molecules per unit formula, with a consequent increase in the proton conductivity curve that reached values as high as $10^{-3} \text{ S cm}^{-1}$ (at 140 °C and 95% RH) and which can be related to the presence of uncoordinated protogenic groups with different acidity. Considering the remarkable proton conductivity, the good thermal and chemical stability, and the small particle sizes, they could be excellent fillers for ionomeric membranes for fuel cell applications.

[1] M. Taddei, A. Donnadio, F. Costantino, R. Vivani, and M. Casciola, *Inorg. Chem.* 52 (2013) 12131.

Poster Presentations

P1

MOFs as crystalline sponges for trapping nicotine and other APIs

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Metal Organic Frameworks are a wide class of crystalline porous polymers built from metal ions and organic ligands. Nowadays MOFs are studied in many fields ranging from catalysis to trapping or storage of gases, such as hydrogen, methane, CO₂ etc. The aim of our research is the molecular confinement of liquid guests of biological relevance inside MOF pores. For this purpose, we chose the structurally related MOFs HKUST^[1], PCN-6^[2], PCN-6^{•[2]}, PCN 777^[3] which are characterized by an increasing porosity and different degrees of interpenetration. The first three networks are formed by copper paddle-wheel nodes of the type [Cu₂(COO)₄] combined with tritopic carboxylic ligands, such as 1,3,5-benzenetricarboxylic acid (BTA) and 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid (TATB), respectively, while the last is assembled from Zr₆ cluster of the type [Zr₆O(COO)₆] with TATB ligand. After activation by solvent exchange method or scCO₂ the MOFs were loaded with the liquid guests. The inclusion processes were monitored by DIP-EI/MS, thermogravimetric and UV/VIS analysis. In the case of PCN-6@nicotine an X-ray structural resolution was performed by synchrotron radiation, freezing the crystal at 100 K. The analysis allowed to recognize nicotine in the electron density maps, showing that the pyridinic ring is coordinated to the copper centers (see figure 1). To the best of our knowledge only few examples of structurally located guest trapped inside MOF were reported in literature.

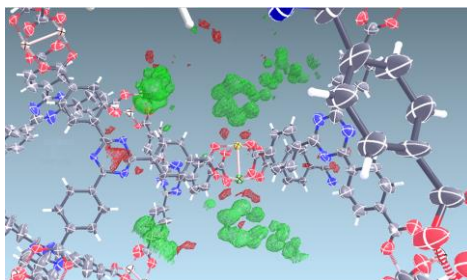


Figure 1: Experimental electron density (green) of nicotine included in PCN-6

[1] A. Navrotsky et al., *Langmuir* 29 (2013) 8140.

[2] H.C. Zhou et al., *J. Am. Chem. Soc.* 129 (2007) 1858.

[3] H.C. Zhou et al., *Angew. Chem. Int. Ed.* 54 (2014) 149.

P2

Selective fluorescence sensing of uracil-containing molecules with a dizinc(II) complex.

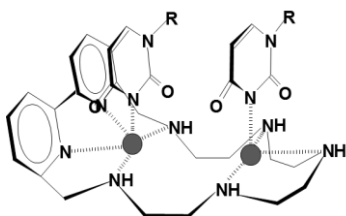
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Selective binding of nucleobases and nucleosides is involved in a number of biological processes including protein synthesis, genome duplication, and signal transduction[1]. Nucleobases/nucleosides derivatives can also be potent pharmacological agents. They actually play a crucial role in the current treatment of cancer and viral infections as the primary components of highly active anti-retroviral therapy. As a consequence, there is a current interest in the design and synthesis of new receptors able to recognize specific, isolated, nucleobases.



Scheme 1

In the course of our study on polyamine ligands containing heteroaromatic units as fluorescent receptors for both metal cations and anions, we synthesized receptors L,[1] which contains a pentaamine chain linking the 6,6' positions of bipyridine. Its dizinc complex, $[Zn_2L]^{4+}$ features two metal ions not coordinatively saturated by the ligand donors, which can act as binding sites for exogenous substrates,

including nucleobases. As a matter of fact, this complex is able to detect uridine and the dinucleotide UpU over other nucleotides or dinucleotides not containing the U unit, thanks to the formation of an exciplex emission at 560 nm[1]. This study has been also extended to pharmacologically active molecules, such as 5-FU and AZT, in order to test the possible use of the $[Zn_2L]^{4+}$ complex as chemosensor for drugs in biological matrices. At the same time, we have coupled time-resolved fluorescence emission measurements and DFT calculations on the complexes formed by U, UpU, UpA, AZT and 5-FU, with the final purpose to give an interpretation on the origin of the exciplex emission observed upon U-containing substrate coordination to the metal centers. The observed exciplex emission has been related to the formation of 1:2 adducts between $[Zn_2L]^{4+}$ and the substrates, containing arrays of three adjacent heteroaromatic units, as sketched in Scheme 1.

[1] C. Bazzicalupi et al., *Chem. Commun.* (2008) 1230.

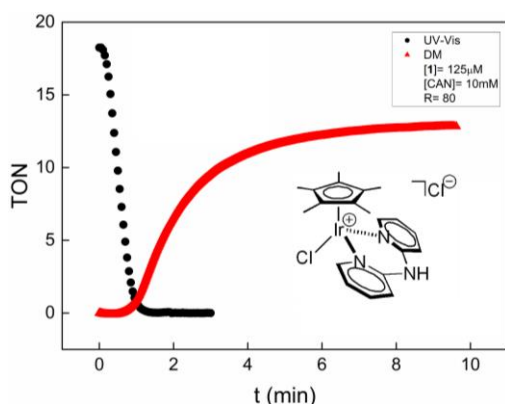
P3

Comparing the catalytic activity of Cp*Ir catalysts with bpy and dpa: insights into the mechanism of water oxidation driven by CAN

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The rapid depletion of fossil fuels asks for the utilization of alternative and sustainable energy sources. Among them, the sunlight has attracted great attention especially as for the realization of a photosynthetic apparatus aimed at producing solar fuels, exploiting the electrons coming from the catalytic oxidation of water to O₂ [1]. Unfortunately, the performances of water oxidation catalysts (WOCs) reported in the literature [2], are far from those required for real applications.



Cp*Ir complexes (Cp* = 1,2,3,4,5-pentamethylcyclopentadiene) are highly active and robust WOCs and their performances can be easily tuned by the choice of the ancillary ligand. Herein we report the study of the catalytic behavior of [Cp*Ir(dpa)Cl₂] (dpa = 2,2'-dipyridilamine) (1) using CAN (cerium ammonium nitrate) as sacrificial oxidant. The performances of 1 were strictly compared to those of its analogous [Cp*Ir(bpy)Cl₂] (2) previously reported

by us [3,4]. The presence of the –NH bridge substantially increases the activity of 1 (up to 6 times) if compared to that of 2; this led us to carry on deeper kinetic studies, in order to rationalize such difference. Those studies shed some new insights on the reaction mechanism of water oxidation driven by CAN in general. Indeed, they clearly showed that CAN is consumed before the oxygen evolution starts (Figure 1), thus suggesting a mechanism proceeding through the formation of an intermediate species that maintains the oxidative power of Ce⁴⁺ or traps the preformed O₂. We believe that such a mechanism might be quite general, since similar results were observed for other molecular catalysts and also for IrO₂.

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P4

Columnar stacking materials based on donor/acceptor complexes of tetrathiofulvalene/coinage-metal metallocycles

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Tetrathiofulvalene and dibenzotetrathiofulvalene, TTF and DBTTF respectively, are strong one- or two-electron donors,[1] whereas a class of cyclic trinuclear coinage complexes, in which the bridging ligand is a 3,5-pyrazolate disubstituted with electron-withdrawing groups, are known to be electron-acceptors.[2] Recently, we have proved the electrophilic behavior of the $[\text{Ag}(3,5\text{-(NO}_2)_2\text{pz})]_3$ cyclotrimer towards small volatile organic or inorganic molecules (e.g., NH_3 , acetone, acetonitrile, pyridine, and dimethylsulfide). This behavior was compared to that of $[\text{Ag}(3,5\text{-(CF}_3)_2\text{pz})]_3$ and rationalized in terms of inter-trimer bonding energies.[3] Moreover, electron-rich trinuclear metallocycles were observed to react with electron-poor organic counterparts, such as TCNQ (7,7',8,8'-tetracyanoquinodimethane). In order to obtain new classes of materials with potentially-interesting conductive properties, reactions between reactants having these opposite donor/acceptor characteristics have been carried out and reported herein. By mixing solutions of the corresponding Au, Ag or Cu trinuclear derivatives and TTF or DBTTF, the formation of the relative adducts was observed. The compounds were characterized by elemental analysis, IR, ESI-MS, and ^1H NMR spectroscopy. Moreover, the X ray diffraction structure determination was performed on suitable crystals of the $[\text{Cu}(3,5\text{-(CF}_3)_2\text{pz})]_3 \cdot \text{DBTTF}$ complex. This compound is mostly stable both in the solid state and in solution as highlighted by ^1H and ^{19}F NMR, and by UV/visible spectroscopies. The $[\text{Ag}(3,5\text{-(CF}_3)_2\text{pz})]_3 \cdot \text{DBTTF}$ and $[\text{Au}(3,5\text{-(CF}_3)_2\text{pz})]_3 \cdot \text{DBTTF}$ analogs have been isolated and their characterizations suggest similar structures in the solid state, but less stability in solution. The $[\text{Ag}(3,5\text{-(NO}_2)_2\text{pz})]_3$ metallocycle shows a stronger interaction with both TTF and DBTTF, readily attaining highly-colored precipitates, albeit with too low solubility for single-crystal XRD analysis.

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P5

Azolate/phosphane Gold(I) compounds in antiproliferative therapy: a new frontier for the azolate gold(I) chemistry

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Azolate gold(I) phosphane compounds have become good candidate for anticancer applications.[1] It was highlighted that azolate gold(I) phosphane compounds were mostly very active in the regards of many panel of cancer cells, in addition to cisplatin resistant cells. Moreover, inhibition studies of pivotal enzymes, such as the seleno dependent ThioredoxinaReductase (TrxR), and an enzyme involved in DNA synthesis such as DeHydroFolateReductase, were carried out highlighting in both cases IC₅₀ ranging from nano- to micromolar scale, respectively.[1][2] In order to study the effectiveness of these new azolate gold(I) phosphane compounds as potential anticancer agents, different cell viability assays (MTT assays) were performed on a human *in vitro* model of HER2-overexpressing breast cancer: SKBR-3 cells.[3] After this preliminary screening, the most promising and effective compounds were selected to extend the study on A17 cell line, a murine preclinical model of Basal Like Breast Cancer (BLBC).[4] Hence, their efficacy in suppressing BLBC growth *in vivo* was tested and IHC analysis on explanted tumors were carried on. Overall, *in vitro assays* demonstrated a remarkable activity for those compounds having the Ph₃PAu⁺ moiety and substituted imidazolate as coligands. Concerning the *in vivo* study the compounds act significantly delaying tumor growth. Accordingly, IHC analysis revealed a remarkable anti-angiogenic activity associated with a lower expression of proliferative markers and a higher level of apoptotic markers in treated tumours in comparison with controls. Moreover, respect to cisplatin these compounds displayed a lower nephrotoxicity, although their liver toxicity was higher. These promising results open the way to further investigations in order to understand the mechanism of action of these new azolate gold (I) posphane complexes.

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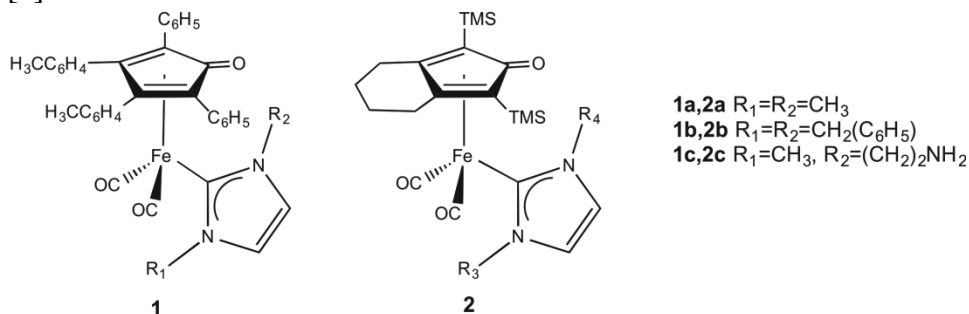
P6

A class of novel iron N-heterocyclic carbene complexes for redox catalytic reactions.

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Catalytic hydrogenation and transfer hydrogenation are among the most important reactions in organometallic catalysis. In recent years, cyclopentadienone iron complexes have drawn attention in this field of chemistry due to their air-water stability, availability from cheap starting materials, and unique catalytic features arising from the presence of a non-innocent ligand.[1] Herein, we report the synthesis and characterization of new carbonyl iron complexes combining different ligands, such as cyclopentadienones and N-heterocyclic carbenes (NHC). The unique features of both ligands have been exploited to obtain new metal-ligand bifunctional catalysts to be employed in hydrogenation and transfer hydrogenation, and to be compared with analogous ruthenium complexes previously investigated [2].



Carbene coordination occurred through a straightforward transmetalation reaction from the silver carbene intermediate (prepared *in situ* from the corresponding imidazolium salts) to the dicarbonyl acetonitrile iron intermediate (obtained *in situ* from the corresponding tricarbonyl complex) leading to complexes **1** and **2**.

Moreover, a microwaved-assisted method for the synthesis of tricarbonyl precursors has been developed. Microwave conditions resulted in shorter reaction time respect to the reflux reaction, without decreasing the yield.

All the complexes have been characterized by spectroscopy (NMR, IR, ESI-MS) and X-ray studies.

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P7

Bioactivity of Curcuminoids in Half-Sandwich Ru(II), Rh(III) and Ir(III) Complexes: benefits from cooking to medicine

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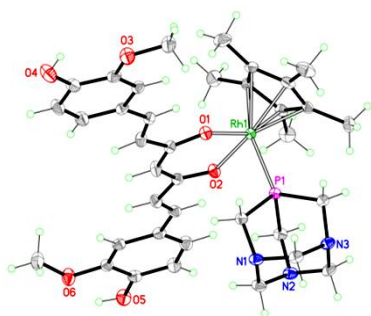
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Curcumin has been used for centuries in Asia as a spice, natural colouring and traditional medicine owing to its anti-inflammatory, antioxidant and antitumoral effects [1].

An alternative strategy to improve the properties of curcumin, without the need to modify the drug, is its incorporation into metal complexes [2].

Ruthenium compounds have emerged in recent years as promising alternatives to platinum drugs by displaying specific activities against different cancers, favorable toxicity and clearance properties [3]. Recently, also metal complexes based on Rhodium and Iridium have arisen as fascinating potential alternative metallodrugs [4].



In the present work we exploit the coordination chemistry of Ru(II) arene and pentamethylcyclopentadienyl Rh(III) and Ir(III) complexes with curcumin [5] and bisdemethoxycurcumin as co-ligands and full characterization of relative RAPTA type complexes with 1,3,5-triaza-7-phosphaadamantane ligand (PTA) [6].

Hydrolysis studies were carried out under pseudo-pharmacological conditions to evaluate their aqueous chemistry.

The antiproliferative effects in two human ovarian cancer cell lines (A2780 and A2780cisR) and non-tumorigenic human embryonic kidney cells (HEK293) will be reported.

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- [2] F.T. Edelmann et al., *Chem Soc Rev* (2015) DOI: 10.1039/c5cs00088b.
- [3] P. Braunstein et al., *Coordination Chemistry Reviews* 270-271 (2014) 31.
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P8

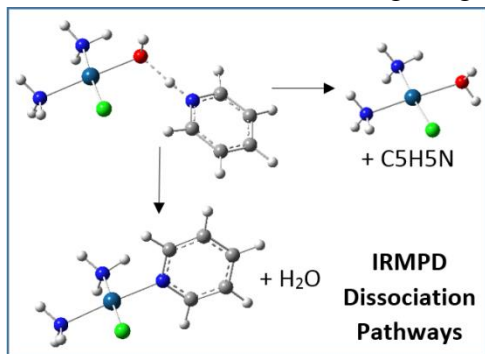
Cisplatin reactions with model biological ligands monitored by IR multiphoton dissociation spectroscopy

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Platinum complexes belonging to the cisplatin family, a widely used antineoplastic drug, are extensively explored in the current literature and sustained effort is devoted to reach deeper insight into the mechanism of their reaction with biological targets and carriers. IRMPD spectroscopy has recently shown great potentiality in the investigation of cisplatin-derived complexes of biological relevance [1-3]. In this contribution mass spectrometry and IRMPD spectroscopy, supported by DFT calculations, are employed to investigate the interactions of pyridine, trimethylphosphate and 4(5)-methylimidazole with the primary intermediate in the hydrolysis of cisplatin, namely the *cis*[PtCl(NH₃)₂(H₂O)]⁺ cation. Ionic products obtained by addition and/or substitution by the selected ligands have been isolated in the gas phase and characterized by IRMPD spectroscopy. The IR spectroscopic analysis has covered both the fingerprint region (1000-2000 cm⁻¹) and the N-H/O-H stretch region (2800-3800 cm⁻¹). The assignment of the vibrational features in the experimental IRMPD spectra has been assisted by computations employing the B3LYP functional, while long range and dispersion effects have been taken into account using the ωB97XD functional.



Direct evidence has been obtained for the substitution reaction of the coordinated water molecule by the selected ligand in the isolated addition complex, activated by the absorption of IR photons. Calculations of the potential energy profile have successfully clarified the behavior of the different complexes.

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P9

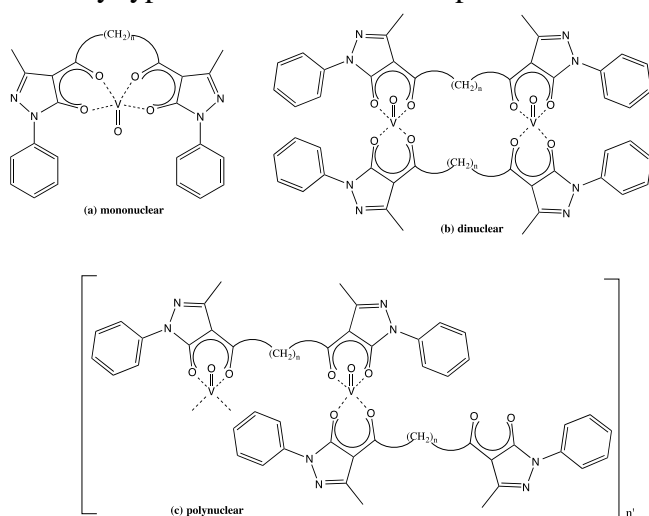
A DFT Study on the stability of novel polynuclear oxovanadium based complexes with acylpyrazolone donor ligands

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Structural investigation of the binding modes of the ligands in transition metal complexes is of great interest due to their effect on the topologies and propagation of extended coordination compounds. This area of research has evolved rapidly in recent years because the coordination compounds may have interesting properties and applications, e.g., DNA binding, cleavage and other biological applications, or used for the design and synthesis of molecular based materials. Coordination chemistry of 4-acyl pyrazolones has been largely investigated for the construction of many types of coordination compounds and for synthesis of biologically active



complexes. Their metal complexes have been found to display catalytic performance [1], biological activity and photochromic properties.

Following our ongoing interest [2] and with the aim of modeling reactive moieties and relevant intermediates on the surfaces of vanadium oxide based catalysts to be used, for example, in the oxidation of organic substrates, mono- and dinuclear oxovanadium complexes, have been recently

synthesized, in our laboratories, based on bis-4-acylpyrazolone donor ligands.

Here, the preliminary theoretical results on the stability of selected novel polynuclear oxovanadium complexes, based on quantum chemical calculations, will be presented.

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P10

Hydroxyapatite nanocrystals and controlled delivery of cisplatin derivatives

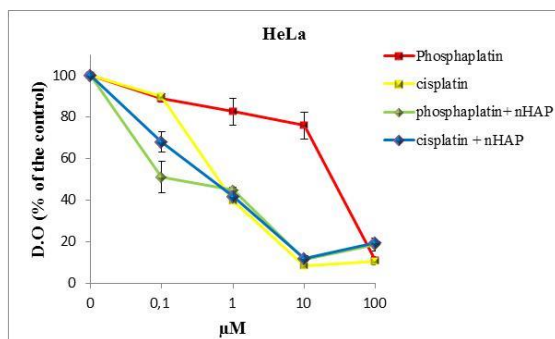
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In last years much attention was devoted to the use of nanoparticles for the modulation of drug delivery. In these studies a lot of interest was addressed to the possible targeted release of drugs and consequent decrease of side effects.

Previous works showed that hydroxyapatite, $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$, nanocrystals (nHAP) can be internalized in tumor cells by endocytosis and that some antitumor drugs with a genomic target can be adsorbed on nHAP [1]. For this reason, the *in vitro* modulation of the antitumor activity for several widely used antitumor drugs, when adsorbed on nHAP, was studied [2]. This new approach could be useful to overcome tumours resistance for antitumor drugs. Recently, *phosphaplatins*, monomeric platinum complexes with a number of phosphates bonded to the metal, were studied for their very



in vitro modulation of the antitumor activity for several widely used antitumor drugs, when adsorbed on nHAP, was studied [2]. This new approach could be useful to overcome tumours resistance for antitumor drugs. Recently, *phosphaplatins*, monomeric platinum complexes with a number of phosphates bonded to the metal, were studied for their very

interesting and pronounced antitumor activity, able to circumvent *cisplatin* resistance of some tumors. The action mechanism of these drugs has been shown to be not genomic [3]. For this reason, we studied the antitumor activity of a model *phosphaplatin*, i.e. $\text{Na}_2\{\text{cis}[\text{Pt}(\text{NH}_3)_2(\text{P}_2\text{O}_7)]\}$, **1**, when adsorbed on nHAP with a platlets shape, by *in vitro* MTT cytotoxicity assays, on different kinds of immortalized cell lines. Interestingly, the adduct between **1** and nHAP (**1**-nHAP), see the Figure, showed a relevant increased cytotoxicity, with respect to complex **1** or nHAP. This suggests the existence of alternative mechanism(s) of cell uptake and/or cytotoxicity induction, due to the combined action of **1** and nHAP.

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P11

Synthesis and thermodynamics of Ag–Cu nanoparticles

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Metallic and bimetallic nanoparticles (NPs) possess unique properties which can provide solutions to engineering problems that cannot be solved with conventional alloyed metals. The chemistry of nanoalloys has been widely investigated to be employed in catalysis, photonics and electronic devices, among many others listed in [1, 2]. Chemical reduction technique is one of the most suitable methods for the NPs synthesis due to its simplicity and because it can assure the sample preparation on a multigram scale [3].

It is well known that the large surface/volume ratio in small or nanosized particle systems has significant effects on their thermodynamic properties and phase relations, and NPs have the melting temperatures (T_M) lower than their bulk counterparts. As far as the T_M depression of binary alloys is concerned, the CALPHAD (CALculation of PHase Diagrams) approach [4] has been extended to calculate nano-sized phase diagrams taking into account the effect of surface energy on the thermodynamic properties of small systems [5]. The Ag–Cu system has been considered suitable as a model to describe the T_M depression as a function of particle size because its binary phase diagram shows a simple eutectic reaction (L (39 at. % Cu) \leftrightarrow (Ag) + (Cu)).

Metallic Ag, Cu, and Ag–Cu nanoparticles (NPs) have been produced by chemical reduction method. The obtained nanoparticles were characterized by powder X-ray diffraction and transmission electron microscopy. A side-segregated configuration was observed for the one-pot synthesized Ag–Cu NPs, and the T_M depression $\sim 14^\circ\text{C}$ was found by differential scanning calorimetry. A comparison between the new experimental data, the literature data on Ag–Cu bimetallic NPs and the corresponding theoretical values obtained from the Ag–Cu nano-sized phase diagram has been done, whereas the melting behaviour of Ag and Cu metal nanoparticles was discussed in the framework of the liquid layer model (LLM).

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P12

Crystal structure and chemical bonding of R_2MGe_6 compounds (R = rare earth metal; M = Mg, Pd)

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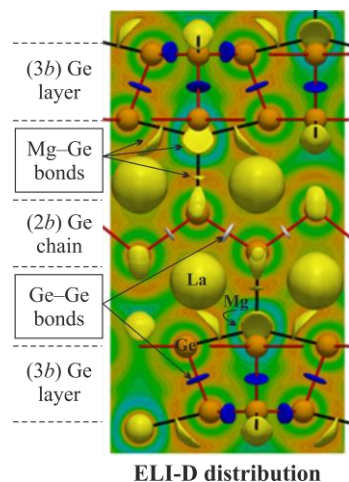
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The R_2MGe_6 polar compounds (R = rare earth metal; M = other metal) are excellent candidates to study the interplays between composition, crystal structure, chemical bonding and properties of intermetallics [1].

In this work we focused on the La_2MgGe_6 and R_2PdGe_6 (R = Y, La–Sm, Gd–Lu) compounds, for which the $oS72-Ce_2(Ga_{0.1}Ge_{0.9})_7$ structural model was established by single-crystal and powder X-ray diffraction data. From the analysis of interatomic distances, “zig-zag” chains of two-bonded ($2b$) Ge (2.44÷2.66 Å) and corrugated layers of three-bonded ($3b$) Ge (2.49÷2.58 Å) bridged by Mg/Pd atoms, were detected.

Moreover, real space chemical bonding analysis was performed: to calculate the effective charges of atoms the Quantum Theory of Atoms In Molecules (QTAIM) [2] was applied; to find “chemical zones” such as bonds and lone pairs the Electron Localizability Indicator (ELI-D) [3] was calculated; to evaluate bonds polarity the ELI-D/QTAIM intersection was constructed.



The presence of covalently bonded ($2b$ and $3b$) Ge species was confirmed. In addition, for La_2MgGe_6 , Mg–Ge strongly polarized covalent bonds were found, allowing to describe this compound as a near Zintl phase, formed by a polyanionic $\infty[Mg-Ge]^{\delta-}$ sublattice balanced by La cations, with a +1.2 positive charge (see figure). Despite the same crystal structure, the Y_2PdGe_6 representative shows an unexpected bonding scenario: Pd atoms are negatively charged (-1.1), ($3b$) Ge are slightly positive and a metal-metal covalent bond between Pd and Y occurs. Further investigations are in progress aiming to elucidate the complex R_2PdGe_6 chemical bonding features.

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P13

New alkynyl-gold(I) complexes featuring anti-cancer activity

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Nowadays, gold complexes have found a relevant position in the field of metallodrugs due to their wide range of pharmacological activities. Encouraging results have been obtained in the treatment of a variety of rheumatic diseases, malaria, HIV and cancer.[1]

The high toxicity that some gold(I), gold(III) and gold nanoparticles have shown against several tumor cell lines inspired the development of a number of structurally different organometallic species being the organic frameworks, constituting the prodrug system, actively involved in determining the overall toxicity of the species. A recent study, by Ott and coworkers, showed that a new family of mononuclear alkynyl(triphenylphosphine)gold(I) complexes, and binuclear analogues, exhibit an important antiproliferative activity in breast adenocarcinoma and colon carcinoma cells.[2] The propargylic sidearm proved to contribute to the overall pharmacological activity of this species and a modulation of this unit could lead to develop more selective and potent candidates for anticancer drugs.

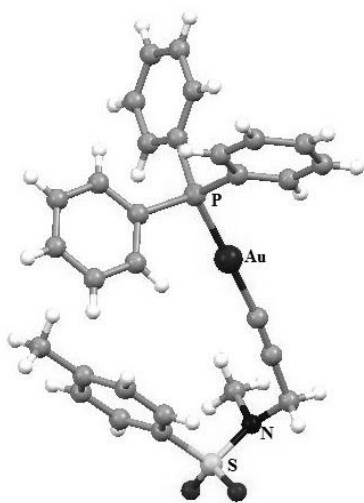


Figure: Molecular structure of **3ab**.

With this aim, a new class of alkynyl-gold(I) complexes, carrying variously substituted propargylic amines, have been synthesized and fully characterized both in solution and solid state. High levels of toxicity (micromolar range) were determined for HT29, IGROV1, HL60 and I407 cancer cell lines.

In particular the lead compound **3ab** was identified as the most active compound in all cell lines (IC₅₀: 1.7-7.9 μM).

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P14

Aromatic Peptide Conjugates as potential MRI contrast agents

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Diphenylalanine (FF), which constitutes the core recognition motif of Alzheimer’s β -amyloid peptide, is able to self-assemble into many different nanostructures from nanotubes to organogels [1]. FF nanostructures have been investigated for their mechanical, electrochemical and optical properties. However, only few studies are devoted until now to investigate their properties for potential biomedical applications [2]. Moreover, the use of FF-based compounds as diagnostic tools remains largely unexplored, overall for the low intrinsic water solubility of these derivatives. Very recently [3], we proposed di-phenylalanine and tetra-phenylalanine conjugates as potential Magnetic Resonance Imaging contrast agents (CAs). These conjugates contain two (F2) or four (F4) phenylalanine residues for self-assembly, a chelating agent, DOTA or DTPA, for achieving gadolinium coordination and an ethoxylic linker at six (L6) PEG units between the chelating group and peptide region. The structural characterization highlighted that only tetra-phenylalanine derivatives keep their capability to aggregate also after the modification of the N-terminus with the Gd-complex. Here we describe two novel peptide CAs based on the aromatic residues 1Nal and 2Nal and indicated as DOTA(Gd)-L6-(1Nal)₂ and DOTA(Gd)-L6-(2Nal)₂. In these conjugates the phenylalanine homodimer is replaced with the 1-Naphtylalanine (1Nal) or 2-Naphtylalanine (2Nal) homodimer. Aggregation properties and relaxometric behaviour of the homodimers, as free bases and as gadolinium complexes, indicate their potential use as MRI contrast agents. Moreover, ¹HNMR studies provides evidence for their capability to encapsulate anticancer drugs such as doxorubicin.

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P15

Solid state luminescence of d^{10} Hg(II) complexes: an integrated experimental and periodic computational approach.

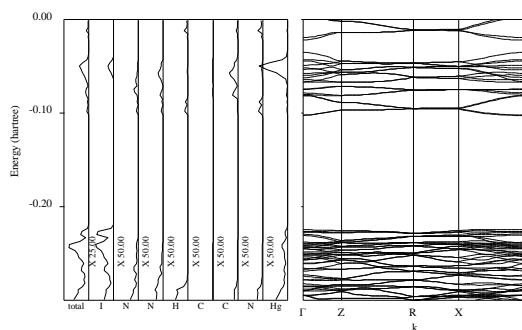
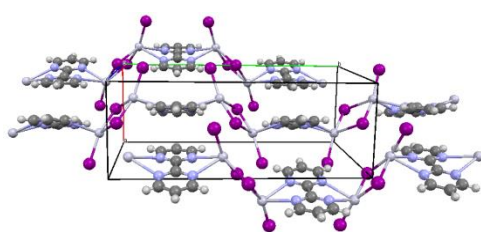
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Luminescent metal complexes of Ru, Os, Pt and Au find many technological applications such as lighting, lasers, sensors. nevertheless in recent years researcher focused in luminescent complexes based on less traditional metal, but showing the advantage of being more abundant and cheaper. A leading role is brought by d^{10} metals because of the versatility of their luminescent levels which can be of ligand centred, charge transfer or, in the case of polynuclear compounds, even metal-centred nature[1].

Most of scientific papers report analysis of luminescence only in a qualitative manner, especially for solid state spectra, and very rarely are rigorous spectral interpretation, because of the difficulty to perform single crystal and polarized spectra. A useful help is obtainable from the computational modeling of crystalline electronic structure now available at reasonable computational cost.

In this communication we report the luminescence properties of a family of HgX_2 (X=halogen or pseudo halogen) coordination polymers or molecular complexes, and 2,2'-bipyrimidine as ancillary ligands. The electronic spectra are interpreted by means of electronic levels obtained from the GTO based periodic package CRYSTAL[2], by employing a DFT approach.



Polymer expansion of $Hg_2I_4(bipym)$ (left) and his band structure and PDOS (right)

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P16

Copper(II) interaction within the N-Terminal domain using a molecular mimic of an A β (1-16) dimer: new insights into the coordination properties of oligomeric A β .

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Alzheimer's disease (AD) is a neurodegenerative disorder characterized by the deposition of extracellular aggregates of 37-42mer amyloid- β peptides (A β).^[1] While in the past A β plaques were identified as the neurotoxic agents in AD, recent findings show that the presence of low-molecular-weight oligomers of A β more closely correlates with neuronal dysfunction.^[2]

Different metal ions accumulate within amyloid deposits, which suggests an involvement of metal ions in AD pathogenesis. Cu(II)-induced A β neurotoxicity might result from changes in the coordination of the metal ion during A β oligomerization or from different peptide/metal ratios.^[3] Copper(II) binding occurs within the N-terminal region, encompassing the amino acid residues 1-16 of A β . We have previously investigated in detail the Cu(II) complexes with A β (1-16) monomers.^[4] We found that the Cu(II)/A β (1-16) system was able to form oligonuclear complexes due to the presence of four independent metal binding sites. As far as we know, little is known on the Cu(II) complex with low-molecular-weight A β species. Here, we report our study on the Cu(II) coordination modes with a synthetic A β (1-16) dimer where the ¹⁶Lys residue, of each peptide chain, is linked to a N,N-bis[(3-amino)propyl]glycine bearing a PEG moiety at the C-terminus. Our results show that trinuclear copper(II) complexes are the major species observed in the range of 2:1 to 4:1 metal to ligand ratio. The Cu/ A β (1-16) dimer revealed a distinct Cu(II) coordination mode with respect to the A β (1-16) monomer. This finding may be of relevance considering the greater toxicity of low-molecular-weight A β oligomers in AD.

Acknowledgments: This work was supported by FIRB-MERIT RBNE08HWLZ.

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P17

Fluoroalkyl Zirconium Phosphates as nanofillers of PFSA based composite membrane for fuel cell applications

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Nanosized layered zirconium phosphate was organically modified with fluoroalkyl chains bonded to the layer surface by reacting the –POH groups with [2,2,3,3,4,4,5,5,6,6,7,7,8,9,9,9-hexadecafluoro-8-(trifluoromethyl)-nonyl] oxirane (hereafter R) to generate P-O-C covalent bonds.

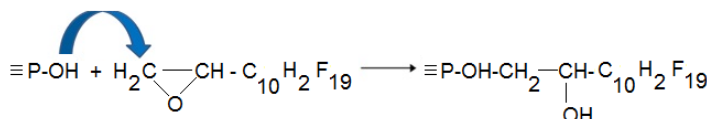


Figure 1. Scheme of reaction.

The hydrophobic nanocrystals thus obtained have planar size of about 20 nm and general formula $\text{Zr}(\text{HPO}_4)_{2-x}(\text{RPO}_4)_x$, with x up to 1.6. These fluoroalkylphosphates are stable in air up to at least 200°C, and show excellent hydrolytic stability in 5M sulphuric acid at 80°C, thus indicating that they are suitable to be dispersed in strongly acidic polymers, such as perfluorosulfonic acids (PFSA). Therefore, the compound with $x=0.9$ was selected to be used as a nanofiller of membranes based on a short-side-chain PFSA in order to mechanically reinforce the PFSA hydrophobic component, so as to improve the membrane lifetime in fuel cell application. Compared to the pristine PFSA, membranes with a filler loading up to 30 wt% show enhanced mechanical properties, in terms of elastic modulus and yield stress, and the largest improvements are observed for the membrane with 10 wt% filler loading. Unexpectedly, this composite membrane exhibits higher proton conductivity than that the unmodified PFSA and better fuel cell performance at 80°C and 33% relative humidity.

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P18

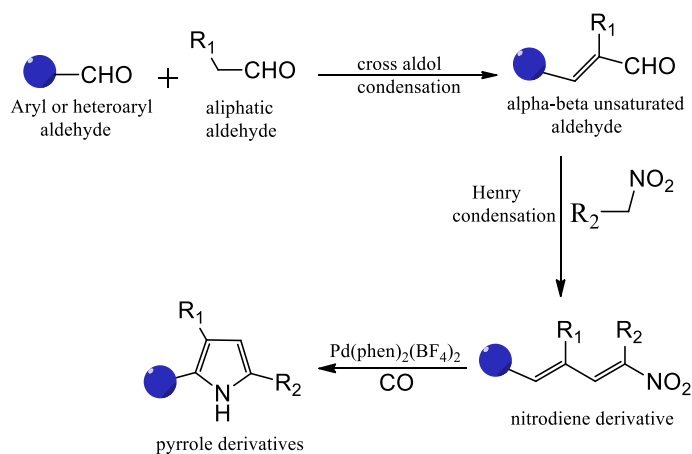
Synthesis of Some Pyrrole Derivatives by Reductive Cyclization of Nitrodiene Catalyzed by Palladium Complexes and with Carbon Monoxide as the Reductant.

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The reductive condensation of a nitro and an olefin group is an extremely powerful method for the construction of heterocyclic rings [1]. As a contribution in this field, we recently used this methodology to prepare some derivatives of thienopyrrole. In continuation to the previous work, here we report a facile and efficient synthesis for some pyrrole derivatives by reductive cyclization of nitrodienes, using palladium/phenanthroline as the catalyst and carbon monoxide as the reductant. The reaction proceeds through the activation of a diene C-H bond in delta position relative to the nitro group. The optimized reaction parameters for the Pd-catalyzed reductive cyclization of 1-(thien-2-yl)-2-nitropropene to 4H-5-methyl thieno[3,2-b]pyrrole, were employed as starting point to test the new catalytic pyrrole synthesis. The nitrodienes were easily accessible by a two step synthesis: 1) cross aldol condensation between two aldehydes only one of them containing alpha hydrogens, to give alpha-beta unsaturated aldehyde, 2) Henry condensation of the so obtained unsaturated aldehyde with nitroalkane to give corresponding nitrodiene.



[1] F. Ferretti, S. Muto, M. Elatawy, M. Hagar, E. Gallo and F. Ragaini, Submitted.

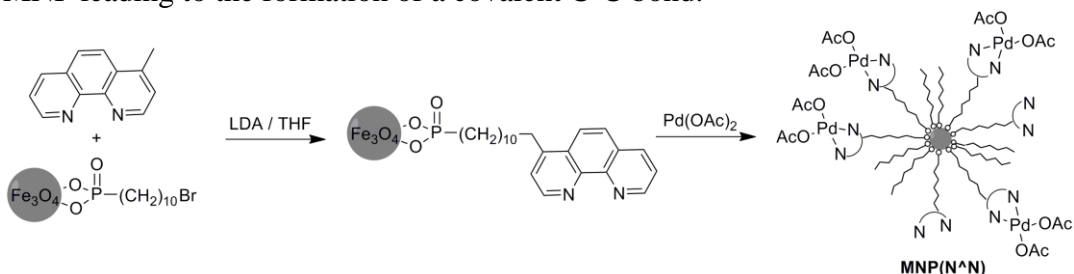
P19

Ferrite Magnetic Nanoparticle for the Recycle of Palladium/Phenanthroline Catalytic Systems.

Francesco Ferretti, Lilian Ansaloni, Fabio Ragaini

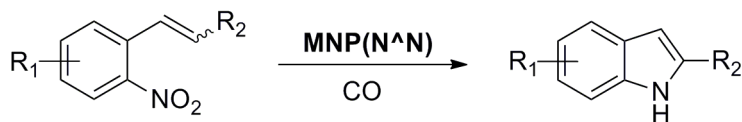
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In the last decade magnetic nanoparticles (MNP) have been widely used as a support for the immobilization of homogeneous catalysts. The small size of these particles allows their thorough dispersion in the reaction media thus nearing the homogeneous environment of soluble catalysts. At the same time their magnetic properties allow to easily recover the catalyst at the end of the reaction. In our group we developed a method with high reproducibility for the synthesis of ferrite MNP functionalized with a phosphonic acid bearing a halogen in the ω position to allow further modification. Owing to our interest in carbonylation and reductive cyclization reaction of nitro compounds, catalyzed by palladium/phenanthroline complexes [1-3], we functionalized the protecting layer with a phenanthroline ligand. A lithium salt of 4-methylphenanthroline was reacted with the protected MNP leading to the formation of a covalent C-C bond.



The achievement of the functionalization was checked by treatment of the functionalized particle with $\text{Mo}(\text{CO})_6$ observing the formation of $\text{Mo}(\text{CO})_6(\text{N}^{\wedge}\text{N})$ complex on the particle protective layer by IR spectroscopy.

$\text{Pd}(\text{OAc})_2$ was then immobilized on the $\text{MNP}(\text{N}^{\wedge}\text{N})$ and the catalyst tested in the cyclization of nitrostyrenes to indoles using CO as a reductant [4].



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P20

Homo- and Heterotrinnuclear cyclic complexes of the 11th group metal ions: fifteen years of a golden chemistry

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In the last fifteen years our group has given an important contribution to the development of the synthesis of cyclic trinuclear complexes (CTC) of the 11th group metal ions. Our pioneering studies showed that trinuclear cyclic gold(I) complexes with bridging imidazolate or carbeniate ligands can act as π -Lewis base. The interaction of these substrates with metal ions, organometallic compounds or organic molecules showing some Lewis acidity, yield polymeric supramolecular structures displaying amazing photoemissive properties. [1] [2] The CTCs can also act as π -Lewis acids: this inversion of the acid/base properties depends on both the ligand and the metal present in the complex; in fact, by using a pyrazolate ligand bearing withdrawing groups (such as NO₂), and silver(I) ions as connecting metal, we obtained a silver CTC that interact with small molecules having donor atoms in their structure such as acetone, acetonitrile, pyridine etc. and it stacks with naphthalene. [3] Moreover, some years ago we found a synthetic route to obtain the first heteronuclear CTCs. By using different stoichiometry, Au₂^I/Ag^I and Au^I/Ag₂^I CTCs were isolated and structurally characterized. [4] This strategy was applied to yield new heteronuclear Au^I/Cu^I CTCs. The crystal structure of [Au₂(μ -C²,N³-BzIm)₂Cu(μ -3,5-(CF₃)₂Pz)], and of [Au₂(μ -C²,N³-MeIm)₂Cu(μ -3,5-(CF₃)₂Pz)] are reported and the crystal packing indicates the formation of a dimer of heterobimetallic trimers linked by quite long Au-Cu metallophilic bonds with distances of 3.317 Å (Au₂...Cu1B) and 3.232 Å (Au₂...Cu1B), respectively. In this case, on the contrary of what already observed in the case of Ag/Au heterobimetallic complexes, the exchange of ligands occurs too. Their formation passes through a likely π - π acid base interaction, affording to stable stacking products only in the case of {Au(μ -C²,N³-BzIm)}₃{Cu(μ -3,5-(CF₃)₂Pz)}₃. These complexes exhibit fascinating and sophisticated photophysical properties that are dependent on the excitation wavelength and on the temperature.

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P21

Crystal engineering of non-centrosymmetric systems

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Crystalline organometallic compound lacking an inversion center were synthesized starting from acentric reagents by means of two different approaches: use of asymmetric metal center and synthesis with asymmetric ligand.

The first methodology was explored by employing a mixed halide of mercury (II), HgBrI, that crystallize in Cmc2(1) space group [1], and three pyridine-based ligands. This complex was prepared with a new solid state reaction. The second approach was developed by employing the 2-(2'-pyridyl)-1,8-naphthyridine (pyNP), (whose non-centrosymmetric crystalline structure (P2(1) space group) was first determined by us) and several d¹⁰ metals (Hg(II), Pb(II), Ag(I)).

A series of complexes were synthesized and their structure was characterized by means of single crystal X-ray diffraction, Raman, IR and electronic spectroscopy. Complexes with HgBrI and aromatic heterocyclic ligands usually give non-centrosymmetric crystalline structure while those with pyNP tend to be centrosymmetric. The obtained results seem to suggest that the crystalline packing was mainly influenced by the metal center than the ligand. These systems are very interesting materials, because of the intrinsic NLO properties that could be employed in optical and optoelectronic application. [2]

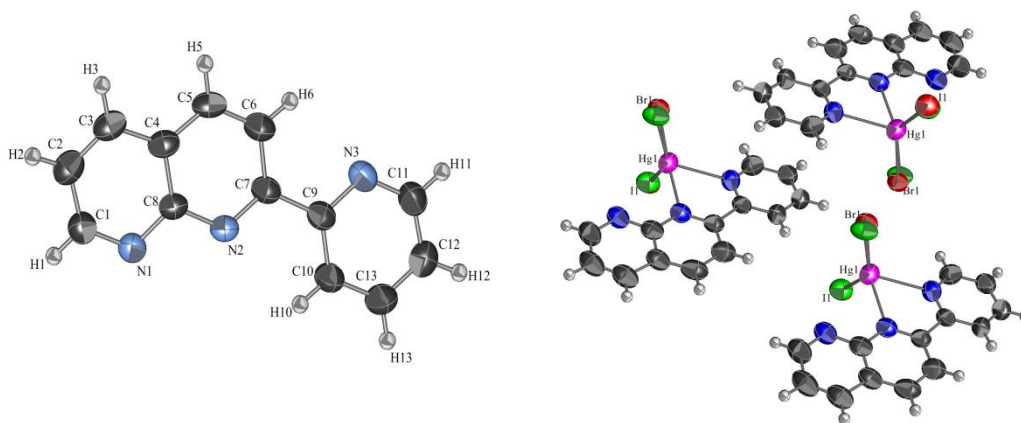


Figure 1 Examples of crystal structures: on the left pyNP, on the right (Hg(pyNP)BrI)

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P22

Synthesis and characterization of novel hydrogen storage materials

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Borohydride- and nitride- based materials exhibit very high hydrogen storage capacities up to 18 wt%, and they also show excellent properties as novel solid room temperature ion conductors or negative electrode materials with improved capacity, thus allowing for very high energy storage densities.[1] For commercial use a prerequisite is the cost efficient large scale production from abundant and relatively cheap raw materials combined with scale-up-ability, and to demonstrate the techno-economical readiness on the prototype scale. The objectives of our study are therefore to obtain a fundamental understanding of metal hydride based energy storage materials, and to develop them towards industrial implementation, achieving high technical performance as well as cost effectiveness. One of the target on energy storage materials is the development of novel metal borohydrides in combination with nitrogen based hydrides, in order to obtain species having high hydrogen densities, low decomposition temperatures, high ion conductivities at low temperatures, and high electrochemical capacities.

A series of new hydrogen storage materials based on the complex hydrides have been synthesized and fully characterized by XRD, TGA, HP DSC, Raman, solid-state NMR, electrochemical techniques (voltammetry, impedance spectroscopy) and modelling (calphad, QE). An integrated experimental-theoretical approach for the solid-state NMR investigation of metal hydrides and borohydrides, mainly focusing on the computation of the ^1H , ^{23}Na , ^{11}B , and ^6Li SSNMR parameters by means of the GIPAW method has been also developed.[2]

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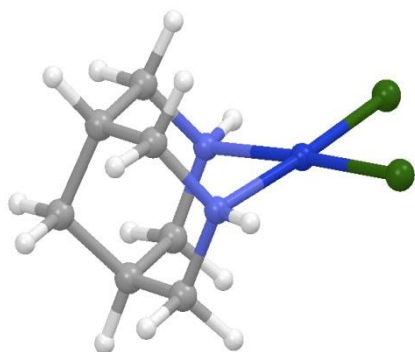
P23

Activation and Reactivity of a Bispidine Analogue of Cisplatin: A Theoretical Investigation

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We carried out a theoretical study to investigate the reactivity of a bispidine, 3,7-diazabicyclo[3.3.1]nonane, analogue of cisplatin, a new anticancer drug with promising properties, to clarify the in vitro reactivity and in vivo mechanism of action of this compound. Thermodynamics and kinetics of the first and second aquation steps and of the reaction of the generated mono and diaquo species with guanine, the main target of the platinum based antitumor compounds, have been investigated. In agreement with the experimental evidence, the bispidine analogue is significantly less reactive than cisplatin toward aquation but the formed aquospecies show a good reactivity with guanine consistently with the promising anticancer properties of these new compounds.



good reactivity with guanine consistently with the promising anticancer properties of these new compounds.

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An Efficient and Recyclable Water Oxidation Catalyst Obtained by “Diluting” Ir(III) into a ZnAl LDH Structure

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Water oxidation is the bottleneck for the realization of an apparatus for the splitting [1] of water into H₂ and O₂, since it is endoergonic and difficult from the kinetics point of view [2]. For this reason it is necessary an efficient catalytic system for water oxidation. Nowadays, many iridium(III)-based complexes and materials able of catalyze water oxidation in presence of a sacrificial oxidant have been reported [3]. Herein, we show that a zinc aluminum iridium Layered Double Hydroxides (LDH), of chemical formula [(Zn_{0.667}Al_{0.306}Ir_{0.027})(OH)₂]Cl_{0.333}•0.4H₂O (**1**) (Fig. 1), is a robust and efficient water oxidation catalyst. LDHs are a family of synthetic

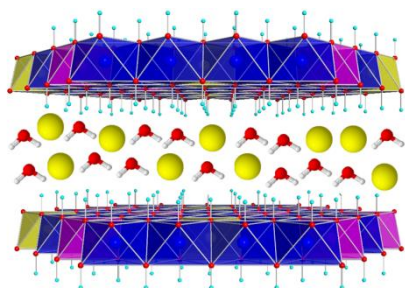


Fig. 1 Layered structure of ZnAlIr LDH 1

layered material that consist of stacked brucite (Mg(OH)₂)-like layers, where some of the divalent cations are isomorphously substituted by trivalent ions, affording positively-charged sheets with charge-balancing anions between them [4]. The ZnAlIr LDH was prepared by the coprecipitation method starting from the chloride salt of the metal cations. The X-ray pattern shows good cristallinity and the typical reflections of ZnAl LDH in the chloride form.

EDX and TEM images show that iridium is uniformly distributed throughout the particles, suggesting that the distribution of the Ir(III) ions in the LDH is homogeneous. The catalytic activity of ZnAlIr LDH toward water oxidation was evaluated using NaIO₄ as sacrificial oxidant. The kinetics was followed by measuring the evolved oxygen in the gas phase through differential manometry. The material exhibits a mean TOF of 2min⁻¹ in unbuffered solutions and 20min⁻¹ in phosphate buffered solutions at pH 7.7. Moreover, it does not show any loss of activity after eight consecutive catalytic runs, completing more than 2160 cycles.

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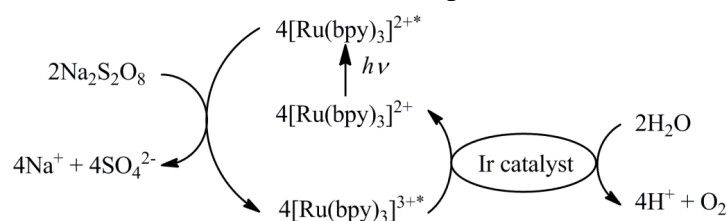
Photocatalytic Water Oxidation with Iridium Catalysts Under Visible Light

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The realization of an efficient apparatus for artificial photosynthesis, aimed at producing solar fuels, is strongly hampered by the difficulty of oxidizing water. Although several iridium complexes have demonstrated to be competent catalysts for water oxidation driven by chemical sacrificial oxidants [1], such as cerium ammonium nitrate (CAN) or sodium periodate (NaIO₄), in only one case has their photocatalytic activity been documented [2]. The classical protocol to explore possible photocatalytic activity stems on combining [Ru(bpy)₃]²⁺ as a photosensitizer and [S₂O₈]²⁻ as an electron acceptor as illustrated below [3].



Scheme 1 Representation of a photoactivated cycle for water oxidation.

In this contribution, we report the results of a systematic study aimed at developing highly active molecular iridium photocatalysts and possibly correlating structure/performance using only the [Ru(bpy)₃]²⁺/[S₂O₈]²⁻ system. Generally speaking, all catalysts were found to be active and O₂ evolution occurred immediately after irradiation of the solution. Chemical and quantum yields varied in the ranges of 35–89%, based on the consumption of persulfate, and 7–22%, respectively, depending on the nature of ancillary ligands bonded at iridium.

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P26

Copper and proteasome: common underlying mechanisms for cancer and neurodegeneration

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Copper is an essential element in many biological processes and an increasingly large body of evidence delineates how its (dys)homeostasis play a critical role in many disorders including cancer and neurodegeneration. The ubiquitin proteasome system (UPS) regulates protein turnover in cells and its derangement is related to both tumorigenesis and neurodegenerative diseases, yet in different context and directions.[1] There are several studies connecting copper to the UPS. For example, some reports have described the interaction of ubiquitin with copper.[2] Moreover, copper complexes inhibit the proteasome for unknown mechanisms suggesting that copper may regulate the UPS at multiple levels.[3] However, many aspects of cell signalling changes modulated by copper–proteasome interactions are still unknown. Here, we address these issues by combining tube tests with assays on cancerous (HeLa), endothelial (Huvec) and neuronal cell lines. Proteolytic assays based on the release of fluorogenic peptides have evidenced that copper inhibits with similar efficiency (IC₅₀ ~1 μM) the three (ChT-L, C-L and T-L) peptidase activities of the isolated 20S proteasome. Native gel electrophoresis performed on isolated 20S proteasome incubated with 20-80 μM Cu(II) evidenced that copper could not disassemble the CP. In HeLa cells either luminometric or fluorometric assays on cell lysates have evidenced a rather paradoxical effect of copper that seems to activate the 20S activity at concentrations higher than 80 μM. These data parallel Western Blot results where no accumulation of polyubiquitinated proteins is observed on increasing Cu(II) concentration. By contrast, this effect was not evident either in HUVEC or in neuronal cells. It is hoped that this work will provide a valuable insight into copper as a key signal regulator and stimulate further research to promote our understanding of copper in disease and therapy.

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[2] G. Arena et al., *Inorg. Chem.* 52 (2013) 9567.

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P27

Bidentate heteroditopic diNHCs: an original class of ligands for transition metal complexes

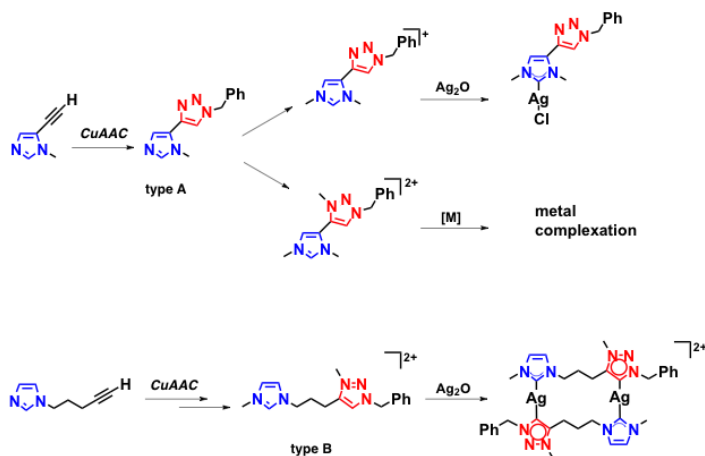
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Di(N-heterocyclic carbene) ligands (diNHC) and related transition metals complexes have become very popular in recent years;¹ most examples on this topic deal with two imidazol-2-ylidenes moieties, the so-called *normal* NHCs, linked by variable bridging groups. Recently, heteroditopic ligands with two different types of NHCs, like mixed imidazol-2-ylidene/1,2,3-triazol-5-ylidene ligands (*n*NHC/*tz*NHC), have been reported. The ligand precursors can be easily obtained by click chemistry (CuAAC)^{2,3} starting from an imidazole functionalized with an alkyne derivative.



Here we present our recent results on this topic: two different classes of ligands have been synthesized, which differ for the position of the triazole moiety, on the backbone of the imidazole ring (type A) or in the nitrogen wingtip substituent (type B).

The related Ag(I) complexes have been obtained by reaction of the ligand precursors with silver(I) oxide; in turn, the carbene ligand can be transferred successfully to other metal centers (Au(I), Cu(I) and Ru(II)). Finally, preliminary results on the anti-proliferative activity of these complexes will also be presented.

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[3] S. N. Sluijter et al., *Organometallics* 33 (2014) 6389.

P28

Non classical diimine ligands for molecular catalysts based on VI Group transition metals for electroreduction of CO₂

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The electrocatalytic conversion of CO₂ into higher energy carbon products is nowadays very attractive for its environmental and economic implications, due to the transformation of a low reactivity species into renewable fuels. In recent years, scientific research has primarily directed towards the discovery of new efficient organometallic molecular catalysts, containing abundant and cheap transition metals. The majority of the published studies is mainly focused on the catalytic activity of Group VII metal-based molecular systems (Mn(I)¹, Re(I)²), whereas much less attention has been paid on the possible usage of complexes with Group VI transition metals (Cr, Mo and W) as electrocatalysts for CO₂ reduction, although many examples from biology and organometallic science could support this idea³.

In agreement with this were synthesized some tetracarbonyl Group VI metal-based coordination compounds containing polypyridyl ligands, [M⁰(CO)₄(L)] (M=Mo, W; L=2,2'-bipyridine and derivatives; 2,2'-dipyridylamine). The peculiarity of these new complexes is represented by low oxidation state and the presence of non classical diimine ligands. The electrocatalytic capability of Mo- and W-based tetracarbonyl catalysts with the 2,2'-dipyridylamine (dpa) ligand in acetonitrile was studied and they were compared with analogous tungsten compounds containing 4,6-disubstituted 2,2'-bipyridyl derivatives. These last compounds showed the doubly reduced species with modest catalytic activities under CO₂, whereas the first complexes showed the activation of an alternative one-electron pathway at potentials close to that of the second reduction of similar complexes containing polypyridyl ligands, thus providing higher CO₂-reduction activity⁴.

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[2] J. Hawecker et al., *Chem Comm* (1984) 328.

[3] T. Reda et al., *Proc. Nat. Acad. Sc.* 105 (2008) 10654.

[4] Franco et al., *ChemElectroChem* (2015) DOI: 10.1002/celec.201500115

P29

Synthesis, Characterization, Catalytic Activity and Biological of New Arylhydrazones of Barbituric Acid Complexes with Co(II), Cu(II) and Ag(I)

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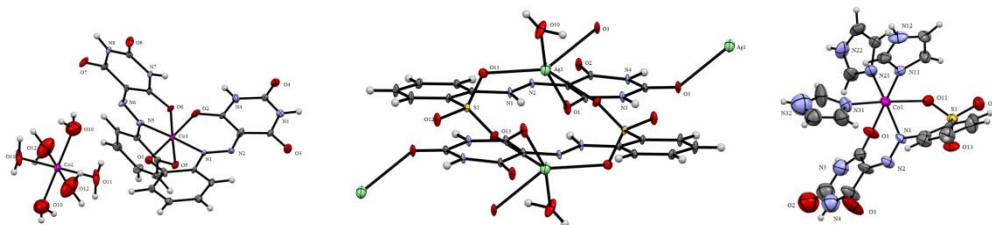
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Derivatives of barbituric acid show very interesting pharmaceutical properties unlike the barbituric acid that is pharmacologically inactive, due to the side group attached to the C5 atom of the pyrimidine ring. One of the most common method used for the functionalization of barbituric acid is the Japp-Klingemann reaction which leads to arylhydrazones of barbituric acid (AHBAs). Their coordination chemistry is still a little explored area of research, notwithstanding their interesting chemical and structural features. Coordination compounds with such ligands are already known, most of them being copper and zinc complexes.¹

Therefore, here we report some novel complexes of Co(II), Cu(II) and Ag(I) containing AHBAs ligand and imidazole as an auxiliary ligand (Scheme). Results toward their catalytic, antimicrobial and biological activities will be also discussed in this report.



Scheme

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Acknowledgements

This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal.

P30

Porous coordination polymers based on the trinuclear triangular $[\text{Cu}_3(\mu_3\text{-OH})(\text{pz})_3]$ (pz = pyrazolate) moiety and bicarboxylate ions.

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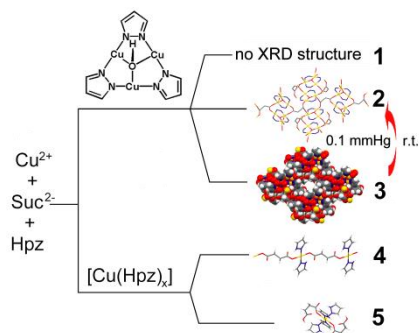
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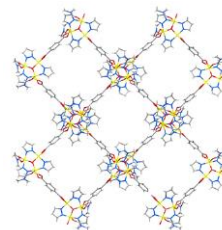
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The reaction of Cu^{II} mono-carboxylates with pyrazole (Hpz) generated a huge variety of CPs all based on the trinuclear triangular Cu^{II} moiety $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ [1]. By employing bi-carboxylates as ditopic anionic linkers, new CPs, in which the trinuclear “clusters” are connected by covalent bi-carboxylate bridges, have been synthesized and structurally characterized. The backbones of thus obtained CPs differ in length, geometry and flexibility, depending on the bi-carboxylate employed. Bicarboxylate-bridged Cu^{II} -pyrazolate have been mainly



obtained from pre-formed $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{MeCOO})_2(\text{Hpz})]$ by exchanging MeCOO^- anions with the desired bicarboxylate dianions, namely succinate, [2] 2-Me-succinate, (S)-2-Me-succinate, 2-dimethylsuccinate, terephthalate, 1,4-phenylenediacrylate, hydromuconate. On the other hand, procedures contemplating the direct reaction of copper bicarboxylates with Hpz have been also employed. In the figures are indicated some results obtained with succinate [2] (left) and terephthalate (right) anions. SC-XRD determinations evidenced that some of these CPs are porous (PCPs) and possess the insolubility normally desired for storage or catalytic purposes. Particularly interesting may be the porosity present in the omochiral PCP bearing (S)-2-Me-succinate.



[1] C. Pettinari et al., *Chem-Eur. J.* 16 (2010) 1106.

[2] C. Di Nicola et al., *Cryst. Growth Des.* 13 (2013) 126.

P31

Inhibition of Alzheimer's amyloid- β peptide aggregation and neurotoxicity by the Trehalose conjugated β -sheet breaker peptide Ac-LPFFD-Th

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In Alzheimer's Disease (AD) the early stages of aggregation of A β peptides initiate a cascade of events in the brain that result in neuronal cell death and consequential cognitive decline. The notion that early soluble A β intermediates are endowed with cytotoxic effects, suggests that a major effort should be directed toward the inhibition of amyloid aggregation at the very early stages.

Thus molecules that interfere with the basic molecular recognition process, preceding the formation of early intermediates, are valuable candidates because they may act, in principle, as therapeutic agents for the treatment of the disease.

We have conjugated a trehalose moiety to the known β -sheet breakers pentapeptides LPFFD.[1] Trehalose has received a special interest because it has been found to be effective in the treatment of neurodegenerative diseases associated with peptide or protein aggregation.[2,3] In this work the ability of the C-terminal trehalose conjugated Ac-LPFFD-Th derivative, to recognize and bind low molecular weight aggregated forms of A β has been investigated by means of different

biophysical techniques including Th-T fluorescence, DLS, ESI-MS and NMR. Moreover, we have obtained evidence that Ac-LPFFD-Th modifies the aggregation features of A β and protects neurons from A β oligomers' toxic insult.

Acknowledgments: This work was supported by FIRB-MERIT RBNE08HWLZ.

[1] P. De Bona, M.L. Giuffrida et al., *J. Pept. Sci.* 15 (2009) 220.

[2] R. Liu, H. Barkhordarian et al., *Neurobiol. Dis.* 20 (2005) 74.

[3] F-F Liu, L. Ji, X-Y Dong, Y. Sun, *J. Phys. Chem. B* 113 (2009) 11320.

P32

Novel symmetrical and non-symmetrical 11th group-NHC complexes: synthesis, cytotoxicity and solution behavior

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As potential anticancer drugs, N-Heterocyclic Carbene (NHC) complexes constitute a recent and fruitful field of research [1]. Our research group, during the last 7 years, has developed different classes of coinage metal-NHC complexes. Recently we have focused the research work on the development of new silver(I)-, gold(I)- and copper(I)-NHCs complexes obtained from the water soluble ligands HIm^{1R,3R}Cl (R = COOCH₃, COOCH₂CH₃ or CON(CH₂CH₃)₂) [2] or the zwitterionic symmetrical NHC ligands NaHIm^{1R,3R,4R''} (R = (CH₂)₃SO₃⁻, R'' = H, CH₃) [3, 4] (Figure 1), NaHBzim^{1R,3R} (R = (CH₂)₃SO₃⁻) and non-symmetrical NHC ligands NaHIm^{1R,3R'} (R = (CH₂)₃SO₃⁻, R' = CH₂C₆H₅), {[HBzim^{1R,3R'}]}Br (R = (CH₂)₃SO₃Na, R' = CH₂C₆H₅) and the related copper(I)- and silver(I)-NHC complexes [4]. We have also investigated the coordination ability of the new ligand {[HTz(pNO₂Bz)₂]}Br towards Ag(I), Au(I) and Cu(I) acceptors [5]. The cytotoxic activity of the NHC complexes has been investigated.

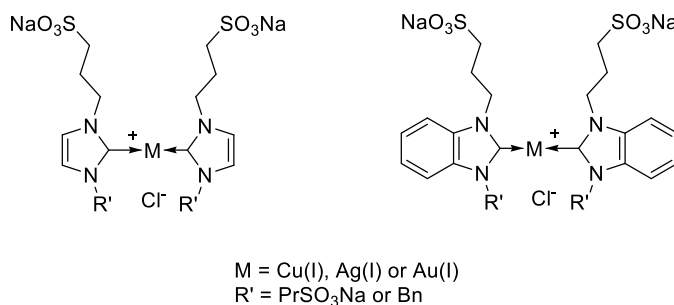


Figure 1: Structures of selected NHCs complexes.

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[3] V. Gandin et al., *J. Inorg. Biochem.* 129 (2013) 135.
[4] M. Pellei et al., *J. Organomet. Chem.* submitted.
[5] M. Pellei et al., unpublished results.

P33

Synthesis, Characterization and Bioactivity of Novel Pentamethylcyclopentadienyl Rh(III) and Ir(III) Complexes Containing Dibenzoylmethane

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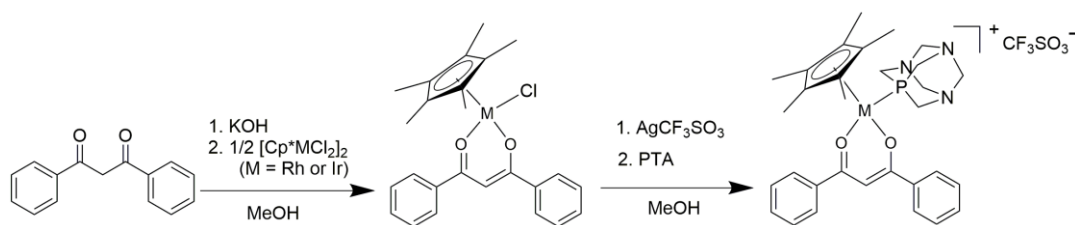
³ Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Organometallic complexes play a key role in medicinal chemistry, especially in the development of anticancer therapies [1]. Among this class of inorganic compounds Rhodium and Iridium complexes are recently attracting an increasing interest in treatment of cancer since they possess several features that make them appealing alternative metallodrugs [2].

Dibenzoylmethane is a natural β -diketone that can be found in small amount in licorice roots. It possesses biological activity against different kind of cancer such as skin, prostate, lung and mammary tumors, lymphomas and leukemia [3].

Pentamethylcyclopentadienyl Rh(III) and Ir(III) complexes bearing dibenzoylmethane and their respective derivatives with PTA (1,3,5-triaza-7-phosphaadamantane) have been synthesized and fully characterized.

Preliminary results on their biological and biochemical activity will also be reported.



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[2] a) C.H. Leung, D.L. Ma et al., *Coord. Chem. Rev.* 257 (2013) 1764; b) W.S. Sheldrick et al., *Inorg. Chim. Acta* 393 (2012) 84; c) Z. Liu and P.J. Sadler, *Acc. Chem. Res.* 47 (2014) 1174.

[3] a) W.B. Harris et al., *Cancer Letters* 178 (2002) 161; b) G.C. Yen et al., *J. Agric. Food Chem.* 57 (2009) 5235.

P34

[HB(pz)₃]Ag(PR₃) complexes as thioredoxine reductase-targeted antiproliferative agents

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Different classes of silver derivatives showed a significant in vitro antitumor activity against a variety of human cancer cell lines, often higher than the corresponding activity of the reference drug, cisplatin. Among them, several silver-phosphino derivatives endowed with significant antitumor activity have been described [1]. We investigated the biological behavior of a series of cationic homoleptic silver complexes of the type [Ag(PR₃)₄]⁺, and we observed that such complexes are able to inhibit significantly TrxR (IC₅₀ for [Ag(PTA)₄](PF₆) = 10.3 nM) [2] suggesting that TrxR, recognized as the most relevant molecular target for gold compounds, could be a protein target also for silver derivatives. This behavior was confirmed for other classes of cytotoxic silver derivatives in particular for water-soluble N-heterocyclic carbene complexes [3].

Stimulated by the appealing results obtained with Cu(I) [4], we moved from the cationic homoleptic silver complexes of the type [Ag(PR₃)₄]⁺, to the synthesis of neutral mixed-ligand [HB(pz)₃]Ag(PR₃) silver(I) complexes (PR₃ = tertiary phosphine). Again, the most effective complex against a wide panel of human cancer cells, including cisplatin and multidrug-resistant sublines, namely [HB(pz)₃]Ag(PPh₃), showed a strong ability to inhibit thioredoxin reductase (IC₅₀ 8.3 nM). In order to find a correlation between the biological activity of silver derivatives and the nature of the phosphino ligands, detailed studies were performed on the stability of [HB(pz)₃]Ag(PR₃) complexes under mass spectrometric conditions.

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[5] M. Porchia et al., *Eur. J. Med. Chem.* 59 (2013) 218; V. Gandin et al., *J. Med. Chem.* 57 (2014) 4745.

P35

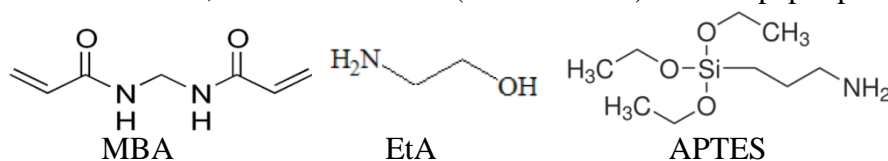
Wood and Paper protection with hybrid inorganic-organic polymers

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The ligno-cellulosic materials (wood and paper) are conveniently used for a variety of human artifacts in virtue of their advantageous characteristics. However, their organic constitution is subjected to physico-chemical and biological deterioration [1]. Here we present the characterization by ESI-MS, NMR, FTIR and μ -Raman spectroscopy of new polyamidoamines designed for the protection of artworks of interest for cultural heritage, in particular of lignocellulosic materials. Polyamidoamines (PAA), functionalized with alcoholic or siloxanic groups (PAAOH or SiPAA), are obtained from N,N-methylenebisacrylamide (MBA) by addition reaction with ethanolamine (EtA) or aminopropyltriethoxysilane (APTES), respectively. SiPAA (an hybrid inorganic-organic polymer) has been tested for wood, whereas PAAOH (wtare soluble) also for paper preservation [2].



Interpenetration of ligno-cellulosic materials by polymers has been monitored by microscopic (ESEM) and spectroscopic (Raman) techniques. The alkoxy silane groups of SiPAA gives hybrid organic-inorganic networking through hydrolysis and condensation reactions (the sol-gel process). In the case of paper, PAAOH was applied in aqueous solution or vehiculated by an Agar gel mainly for deacidification purposes. Preliminary results have shown that the polymer acts as an effective deacidification material without altering chromatic and mechanical characteristics of paper.

Financial support from Renner Italia SpA (Minerbio, BO) is gratefully acknowledged.

[1] R. M. Rowell (Ed.), "Handbook of Wood Chemistry and Wood Composites" (2013), CRC Press, Boca Raton, FL, USA.

[2] L. Bergamonti, E. Chiappini, G. Predieri, S. Palanti, L. Maistrello, "Wood preservative composition" Int. Patent application WO 2015/004590 A1.

P36

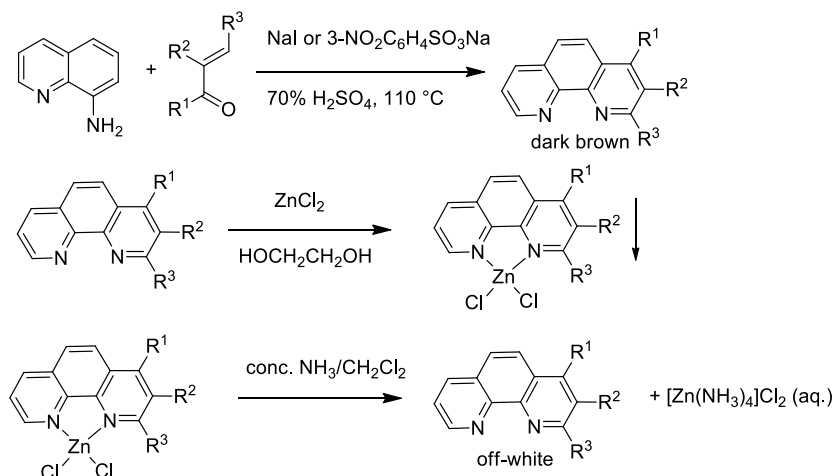
Phenanthrolines: a Non-Chromatographic Purification Method

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The often employed preparation of phenanthrolines by Skraup type condensation reactions almost invariably requires a chromatographic purification of the product. However, chromatographic purification of phenanthrolines is notoriously difficult and strongly limits the scale of the preparation. During our studies on carbonylation reactions of nitroarenes, we became interested in the synthesis of substituted phenanthrolines [1,2]. Based on our previous experience with bis-imine type of ligands [3], we considered that the formation of a (Phen)ZnCl₂ complex may be a step of an effective purification strategy because such complexes are very insoluble, whereas ZnCl₂ complexes of monodentate nitrogen ligands are much more soluble. We obtained impure (dark brown) phenanthrolines by condensation of 8-aminoquinoline with an unsaturated aldehyde in 70% H₂SO₄ and in the presence of either NaI or sodium 3-nitrobenzenesulphonate. Treating the crude mixture with ZnCl₂ in ethylene glycol afforded insoluble complexes from which the free phenanthroline could be obtained in a pure form by treating the complex with concentrated aqueous ammonia and CH₂Cl₂.



[1] F. Ferretti, F. Ragaini, R. Lariccia, E. Gallo, S. Cenini, *Organometallics* 29 (2010) 1465.

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[3] M. Gasperini, F. Ragaini, S. Cenini, *Organometallics* 21 (2002) 2950.

P37

Synthesis and characterization of Co-carbides particles

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Cobalt carbides are interesting materials due to their possible technological applications as permanent magnets [1,2].

Experimental results concerning the synthesis and the characterization of Cobalt and Co-carbides particles will be presented.

Starting from chloride or acetylacetonate cobalt salts, cobalt or carbide particles, respectively, were synthesized by polyol reduction, using TEG (tetraethylene glycol) both as solvent and reducing agent, at the reflux temperature of the solvent, adding oleic acid and oleylamine as protectors.

All the products obtained were characterized by X-ray diffraction (XRD), scanning electron microscopy (FE-SEM), and magnetic measurements (SQUID).

SQUID measurements at room temperature reveal a ferromagnetic behavior for all the phases with an increase of the coercive field from Co to Co₃C. This trend is related to the increase of the pinning centers concentration, thus strongly reducing the mobility of Bloch walls.

[1] K.J. Carroll et al., *Applied Physics Letters* 101 (2012) 012409.

[2] H. Yoon et al., *Phys.Chem.Chem.Phys.* 17 (2015) 1070.

P38

New findings and analyses with non-invasive techniques on paintings by Pietro Alamanno (15th century) held at the Ascoli Piceno Pinacotheca

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Many works by both Carlo Crivelli and Pietro Alamanno have been in the past sometimes mistakenly attributed to one artist or another for a number of reasons, both stylistic and historical. Alamanno's hand was often seen in the works by Crivelli himself, but this has no actual confirmation in the stylistic form or in chronological references. The XRF results provided interesting data that are useful clues with regard to both the type of pigments used, and to the attribution and the stylistic analysis of the paintings when compared to the paintings of known attribution by the artists studied. We investigated the following works by Pietro Alamanno and we compared them with works that were assuredly attributed to the Master Carlo Crivelli. The equipment used for the analysis consists of a Nikon D7000 reflex camera with a CMOS-DX sensor suitably modified for IR radiation. To complete this system, a number of filters that allow to selectively collect different IR frequencies (750 nm, 920 nm) were used. For XRF analyses, the system used was made up of: a Coolidge tube with tungsten anode provided by Italstructures, a high resolution silicon detector from Amptek with associated electronic equipment (MCA) and a pair of laser diodes used to spot the measuring point.



San Giacomo Della Marca



Santa Maria Maddalena



Santa Lucia



Cristo Morto S Rocco e San Sebastiano



Madonna col Bambino in Trono San Nicola Maddalena Giovanni Battista Leonardo

P39

New photoluminescent Zn(II) complexes with O,N,N ligands containing substituted benzo-1,3-diazole heterocycles

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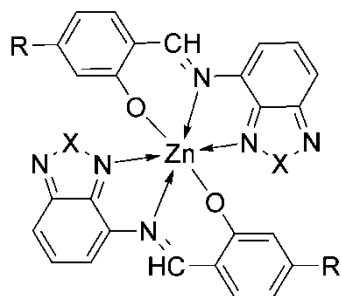
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A new series of salicylaldiminate N,N,O ligands containing substituted benzo-1,3-diazole heterocycles and related zinc(II) complexes were synthesized and characterized [1][2]. The X-ray structure analysis confirmed hexacoordination with participation of the heterocycle to the metal coordination, although the geometry becomes strongly distorted with a long bond length between zinc and the nitrogen atom of the heterocycle. All the synthesized compounds showed



X: S, O, N(CH₃); R: H, OEt, N(Et)₂

photoluminescence properties both in the solid state and in solution. The role of the heterocycle on the spectroscopic properties and the influence of the substituent on position 2 (oxygen, sulfur or methylamino group) and of the electron donor substituents in para to the imininc bond were studied. A general red shift of the absorption wavelength along the N → S → O series and with the increase of the donor strength was evidenced. The wavelengths of emission follow a similar red shift along the N → S → O series. For some complexes the emission is significantly shifted towards the area of the near infrared. High Stokes shifts were observed for both ligands and complexes, increasing with decreasing donor strength. As expected for red/ infrared emitters, photoluminescence quantum yield values of complexes were medium to low, lower in solution than in the solid state. According to preliminary TD-DFT calculations, the HOMO results mainly localized on the donor salicylaldehydic moiety while the LUMO on the heterocyclic acceptor.

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Copper(I) complexes with homoscorpionate tris(azolyl)borate and auxiliary monodentate phosphine ligands: synthesis and *in vitro* and *in vivo* Anticancer Activity

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The research on copper(I,II) coordination compounds as antiproliferative agents is one of the main research lines of our group since years [1]. Hydrophilic, monocationic $[M(L)_4]PF_6$ complexes (M = Cu, Ag or Au; L: thp = tris(hydroxymethyl)phosphine, L: PTA = 1,3,5-triaza-7-phosphaadamantane, L: thpp = tris(hydroxypropyl)phosphine) were synthesized and tested as cytotoxic agents against a panel of several human tumour cell lines also including a defined cisplatin resistant cell line [2]. The best results in terms of *in vitro* antitumour activity were achieved with metal-thp species and, among the coinage metal complexes, copper derivatives were found to be the most efficient drugs [2]. As a natural development of this research line, tetrahedral copper(I) TpCuP complexes, where Tp is a N,N,N-tris(azolyl)borate and P is a tertiary phosphine, have been synthesized and characterized by means of NMR and ESI-MS, and XAS-EXAFS, and X-ray diffraction analyses on the representative complexes $[HB(pz)_3]Cu(PCN)$, and $[HB(3-(NO_2)pz)_3]Cu(PCN)$ [3]. All copper(I) complexes were evaluated for their antiproliferative activity against a panel of human cancer cell lines (including cisplatin and multidrug-resistant sublines). The two most effective complexes $[HB(pz)_3]Cu(PCN)$ and $[HB(pz)_3]Cu(PTA)$ showed selectivity toward tumor vs normal cells, inhibition of 26S proteasome activity associated with endoplasmic reticulum stress, and unfolded protein response activation. No biochemical hallmarks of apoptosis were detected, and morphology studies revealed an extensive cytoplasmic vacuolization coherently with a paraptosis-like cell death mechanism. Finally, the antitumor efficacy of complex $[HB(pz)_3]Cu(PCN)$ was validated in the murine Lewis Lung Carcinoma (LLC) model [3].

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P41

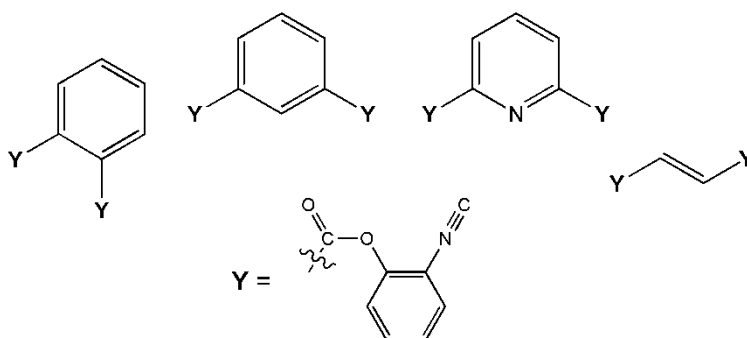
Diisocyanide Pt(II) and Au(I) Complexes: Catalytic Activity and Reaction with Amines

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Despite being studied extensively as ligands with interesting electronic properties such as strong σ -donor and π -acceptor ability [1], isocyanides have more rarely been used in catalysis. [2] In the past, few attempts to increase the stability of their transition metal complexes have been made, mainly by synthesizing chelating di-isocyanide, as reported for the first time by Angelici et al. [3]. In this case, the di-isocyanides were obtained through a long series of steps and in low yields. More recently Naik et al. developed a single-step approach that exploit the ring-opening equilibrium of oxazole derivatives. [4] Following this rationale, we synthesized and characterized a series of di-isocyanide ligands, both chelating and not, by varying the bridge between the two functions and studying its effect on the coordinating modes of the resulting ligands. They have been applied to the synthesis of the both Pt(II) and Au(I) complexes. Some results on their reactivity and their catalytic applications are reported.



The authors wish to dedicate this work to the memory of Prof. Rino A. Michelin.

[1] (a) N.A. Bokach et al., *Coord. Chem. Rev.* 255 (2011) 2946; (b) R.A. Michelin et al., *Coord. Chem. Rev.* 218 (2001) 75.

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P42

Synthesis and ^{13}C $\{^1\text{H}\}$ -NMR Spectroscopy Characterization of the Pt(0) Triangulo-Cluster Derivative $[\text{Pt}_3(\text{CO})_3(\text{PPh}_2\text{Np})_3]$

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The Pt(0) clusters described here are characterized by the presence of trimetallic M_3^1 unit and by a general formula of the type $[\text{Pt}_3(\text{X})_3\text{L}_3]$ with $\text{X} = \text{CO}, \text{SO}_2, \text{RCN}^2$ and $\text{L} =$ tertiary phosphines³. All clusters are 42 valence electrons systems. We have investigated the reaction of $[\text{Pt}(\text{cod})\text{Cl}_2]$ ($\text{cod} = 1,5\text{-cyclooctadiene}$) with naphthyldiphenylphosphine (PNpPh_2) under CO atmosphere to obtain the $[\text{PtCl}_2(\text{CO})(\text{PPh}_2\text{Np})]$ intermediate, that react with Zn dust and forms the complex $[\text{Pt}_3(\text{CO})_3(\text{PPh}_2\text{Np})_4]$. This derivative reacts with H_2O_2 at 50 °C in acetone/dichloromethane solution involving the quantitative oxidation of one PPh_2Np unit⁴. The $^{13}\text{C}\{^1\text{H}\}$ -NMR of the $[\text{Pt}_3(\text{CO})_3(\text{PPh}_2\text{Np})_3]$ complex had not been described so far. The IR data are in good agreement with those reported in literature for (νCO) in similar compounds (terminal CO 1857, 1794 cm^{-1}). As for the $^{31}\text{P}\{^1\text{H}\}$ -NMR data, we considered the four isotopomers: without ^{195}Pt 29.0% (I); with a one ^{195}Pt 44.4% (II); with two ^{195}Pt 22.7% (III) and three ^{195}Pt 3.9% (IV). The central signal of isotopomer (I) presents an A_3 spin system. Isotopomer (II) ($\text{AA}'_2\text{X}$ spin system) show a doublet of triplets assignable to A resonance and are due to the $^1\text{J}_{\text{P-Pt}}$ coupling which is further splitted by two atoms equivalents A'. The doublets of doublet symmetrically arranged in the center of the spectrum are attributable to A' are due to $^2\text{J}_{\text{P-Pt}}$ and $^3\text{J}_{\text{P-Pt}}$ couplings. The interpretation of $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the ^{13}C -enriched complex is similar: the center peak is assignable to isotopomer (I) having spin system A_3 , while the two most intense doublets are due to (II), and in particular to the resonance of the $\text{A}_2\text{A}'\text{X}$ system..

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P43

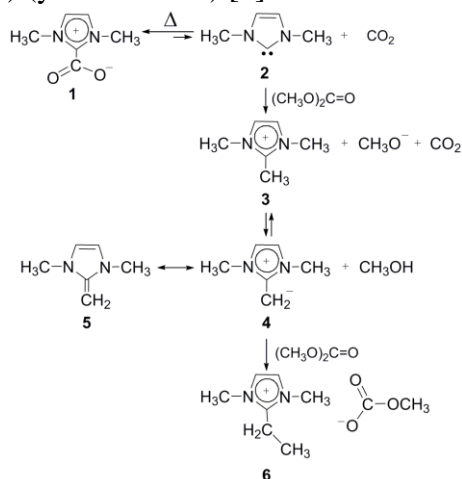
Unexpected 2-ethyl-functionalisation of 1,3-dimethylimidazol-2-ylidene with dimethylcarbonate: Use of the reaction system in organocatalysis.

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Imidazolium based Ionic Liquids (IL) and salts find application in a wide variety of fields including catalysis and advanced materials [1]. We report here the reaction of 1,3-dimethylimidazolium-2-carboxylate (**1**) with dimethylcarbonate (DMC) at temperatures ranging from 180 to 200 °C to yield 2-ethyl-1,3-dimethylimidazolium methyl carbonate salt (**6**) (yield of 75 %) [2].



We propose the mechanistic pathway for formation of product (**6**) involves the following steps: i) decarboxylation of compound (**1**), ii) methylation of the 2-ylidene intermediate (**2**) with DMC leading to the 1,2,3-trimethylimidazolium cation (**3**), iii) deprotonation of the C(2)-methyl substituent of (**3**) affording zwitterion (**4**), iv) further methylation of (**4**) with DMC leading to compound (**6**).

Salt (**6**) has been characterized by ¹H-, ¹³C-NMR and by ESI-HRMS.

The (**1**)/dimethylcarbonate reaction system has been employed in the synthesis of 1,7-heptanedioic acid dimethyl ester from cyclohexanone and DMC.

Project PONA3 00369 “Laboratorio SISTEMA” is gratefully acknowledged.

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[2] C. Annese, L. D'Accolti, C. Fusco, I. Tommasi, *Catal. Commun.* 46 (2014) 94.

P44

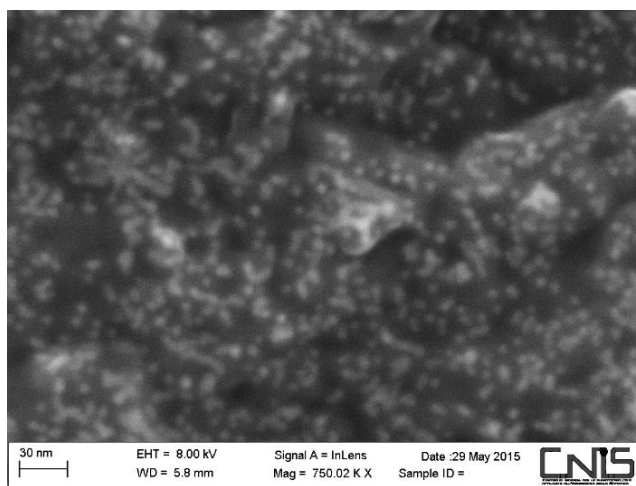
Gold and silver nanoparticles conjugated with Rhodamine B isothiocyanate: synthesis and depth characterization

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Gold and silver nanoparticles (AuNPs, AgNPs) are applied in several field, such as biomedical, sensor, optoelectronics.[1-3] In this framework we report a depth investigation about new synthesized material based on AuNPs and Ag NPs stabilized by two different thiols: 3-mercaptopropansulfonate (3MPS) and 2-ethylaminoethanthiol (DEA).[4-6] The AuNPs and AgNPs (diameter 4-10 nm), were in depth investigated by means of several techniques, (¹H NMR, ¹³C NMR, Uv-visible, FTIR, XPS, DLS, FESEM, AFM). In a second step these nanoparticles are conjugated with a dye, Rhodamine B isothiocyanate (RTC), to obtain a traceable systems, useful for biomedical purposes.



In figure the FESEM image Au3MPSDEA@RTC (diameter 5-7 nm).

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- [4] I. Venditti et al., *Colloids and Surfaces B: Biointerfaces* 131 (2015) 93.
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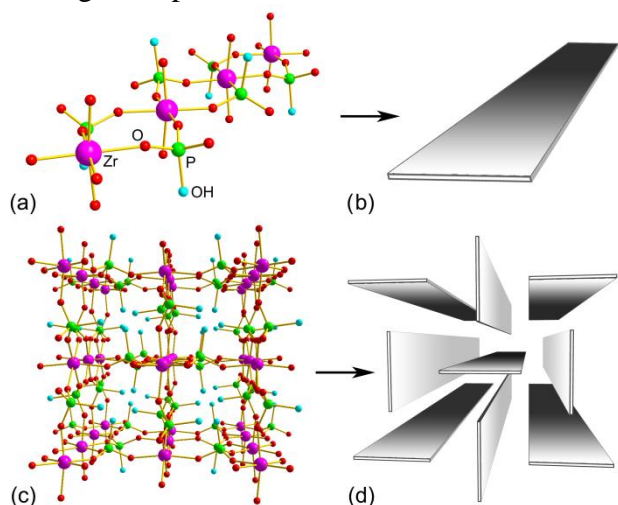
Unusual behaviour of nanocrystalline zirconium phosphates

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Reaction between phosphoric acid and a zirconyl organic salt in aliphatic alcohol media allows to quickly obtain gels based on zirconium phosphate (ZP) nanocrystals with peculiar physico-chemical properties as compared to conventional microcrystalline ZPs [1]. Nanocrystalline ZP can be easily modified towards post-synthesis treatments, allowing the preparation of hybrid zirconium phosphonate compounds by simple topotactic anion exchange reactions [2] and can be easily dispersed within polymer matrices, obtaining polymeric nanocomposites with highly improved mechanical properties [3]. Therefore, the gel procedure represents an innovative, versatile, mild approach for the synthesis of ZP nanoparticles. We recently found that nanosized ZP, obtained from drying the gels, also has a different thermal behaviour than microcrystalline ZP. Nanosized ZP undergoes a phase transition at 120° C with formation of a new ZP phase with a



3D-architecture, whose structure has been solved *ab initio* from X-ray powder diffraction data. It is composed of primary chains, (a) and (b), oriented with their main planes perpendicular to each other, (c) and (d). The present contribution will illustrate the special reactivity of nanocrystalline ZP and its thermal behaviour. The structure of the new 3D ZP phase will be also discussed and compared to that of the already known ZPs.

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Integrin Targeting with Peptide Bioconjugated Nanocrystalline Heterostructures: a Theranostic Prospect

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$\alpha_v\beta_3$ integrin is an important tumor marker widely expressed on the surface of cancer and on tumor-associated endothelial cells [1]. Colloidal inorganic nanocrystals (NCs) exhibit interesting electrical, optical, magnetic, and chemical size dependent properties. The combination of different nanostructured materials enable the access to novel nanomedical platforms for multimodal imaging, and simultaneous diagnosis and therapy, thus offering new and improved opportunities to overcome limitations associated with conventional diagnosis and therapy of cancer. Here, binary asymmetric binary nanocrystals (BNCs), composed of a semiconductor TiO₂ nanorod joined to a magnetic γ -Fe₂O₃ spherical domain, have been embedded in PEG modified phospholipid micelles [2]. These systems, characterized by high photoactivity and magnetic properties, are particularly suited as phototherapy and hyperthermia agents as well as a magnetic probes in biological imaging. A designed peptide containing the RGD motif for targeting of $\alpha_v\beta_3$ [3] has been successfully conjugated with the BNCs. Each step of the work has been thoroughly monitored by means of optical, morphological and structural techniques. Cytotoxicity has been shown only for very high tested concentrations. Confocal microscopy investigation has highlighted the selectivity of the peptide-BNC conjugates for the $\alpha_v\beta_3$ integrin, and, consequently, a high potential of these nanomaterials for theranostic applications.

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P47

In situ generation of a family of substituted thioureas-Cadmium thiocyanate coordination polymers: a crystal engineering study for new topologies and properties.

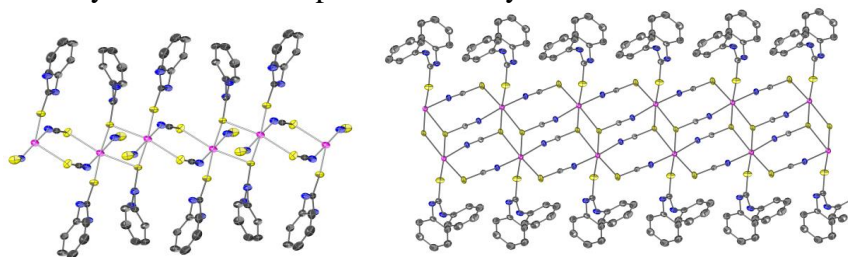
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Cadmium complexes can adopt different coordination typologies, depending on size, electrostatic and covalent bonding forces. Together with versatile ligands as thiocyanate ion is possible to develop an interesting chemical engineering of coordination polymers, because of its ability to act as a monodentate, bidentate or bridging ligand. Some coordination compounds of thiourea and cadmium have been reported [1] and they are of great interest for two main reasons: (i) the non-linear optical (NLO) properties of these compounds [2] and (ii) the convenient preparation of semiconducting materials through the thermal decomposition of these complexes [3].

We have prepared a series of organometallic polymers formed by a cadmium thiocyanate network and substituted thiourea with the aim to analyze the effects of the ligand anisotropy, hydrogen bond and halogens substitution in the ancillary ligands. We have synthesized and fully characterized five new coordination polymers of general formula $\text{Cd}(\text{SCN})_2\text{R}_n$ ($n=1$ or 2) (R =thiourea, N-methylthiourea, N-phenylthiourea, N,N'-diphenylthiourea, N-1,3-difluorophenylthiourea).

The synthesis of these compounds has been optimized by using an *in situ* generation of the cadmium thiocyanate, that induces the growth of big single crystals. These compounds show strong luminescence, and we tried a spectral interpretation by means of a computational analysis.



Polymer expansion of $\text{Cd}(\text{SCN})_2(\text{phtu})_2$ (left) and $\text{Cd}(\text{SCN})_2(\text{ph}_2\text{tu})$ (right)

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Novel Coordination Frameworks Based on Polytopic Heteroaromatic Nitrogen and Carboxylate Ligands

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Metal-organic frameworks (MOFs) are comprised of metal clusters and organic ligands. MOFs, similar to zeolite, carbon nanotubes, and activated carbon, have very porous structures. Since MOFs have many more building blocks than materials such as zeolite, their properties can be finely tuned through a careful choice of the ligands. The functionalization of the MOF could be achieved by modifying ligands before the MOF synthesis (pre-synthetically) or after the synthesis (post-synthetically). These functionalized MOFs can be used for numerous applications such as gas storage, gas separation, and catalysis. The advantage of these hybrid materials, over classical (natural and synthetic) porous species (zeolites, active carbons, silica, etc.) resides in the possibility of easy optimization and fine tuning of their functional properties by using modification or substitution strategies of the organic ligands, and through the choice of suitable metallic ions [1, 2]. Moreover, the simultaneous presence of channels (or cavities) and metal ions capable of catalytic activity makes these materials particularly intriguing as heterogeneous catalysts for the transformation of small molecules, and, if the pores are suitably “decorated”, they can display significant size-, regio-, and enantioselectivity [3-6].

In this work we report the synthesis and characterization of a series of pyrazolyl-based ligands, namely 3,3',5,5'-tetramethyl-1H,1'H-4,4'-bipyrazole (H₂Me₄BPz), 1H-pyrazole-3,4,5-tricarboxylic acid (H₄PzTc), 1H,1'H-4,4'-bipyrazole (H₂Pz) and their MOFs with late transition metals (Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Ru⁺⁺) characterized by the presence of diverse counterions.

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