Chimica Inorganica

INO-PL-01 Mechanisms of action and transport of platinum drugs: an update

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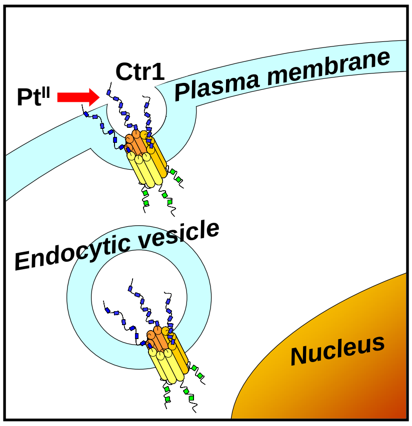
When the antitumor activity of cisplatin was discovered no one would have predicted the existence of specific proteins able to transport platinum across the cell membrane or to specifically recognize DNA modified by this drug. However such proteins do exist and, furthermore, are specific for the platinum substrate considered. [1]

Apart from passive diffusion, a number of carrier-mediated import proteins have been identified, the main players being organic-cation transporters and the copper influx transporter CTR1. Moreover ATPases involved in the removal of excess copper appear to play a role in the excretion/inactivation of platinum drugs. Also the copper chaperone Atox1 has been found to interact with platinum drugs at the same site as copper. Moreover, for longer contact time with platinum, it forms dimers similar to those formed by copper and which have been shown to be able to translocate to the nucleus and act as a transcription factor.

After cisplatin binding to the putative target, double-stranded DNA, a kinked structure is formed that is recognized by certain proteins. Such an interaction has direct consequences on cell viability and eventually leads to cell killing by apoptosis.

In the presentation new insights both in the cellular uptake of the drugs and in the processing of their adducts with DNA will be highlighted.[2,3]



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INO-PL-02 Organometallic Nanoparticles: Growth and Surface Chemistry

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Organometallic nanoparticles are prepared by decomposition in mild conditions of organometallic precursors in solution. The decomposition is preferably achieved under dihydrogen which results in the formation of a clean surface, covered with hydrides and able at performing further chemistry or growth processes. Addition of various ligands may modify both the physical and the chemical properties of the particles as well as the growth process, leading to the formation of particles of defined sizes and shapes, for example nanorods, nanocubes, nanowires of iron and cobalt, nanoarrows or nanocubes of platinum as well as to extended super-lattices of monodisperse nanospheres.

The surface characterization may be achieved by standard techniques of material science as well as by the use of NMR (solid state, solution and gas phase). In this respect, static solid state ^{2}D NMR and MAS ^{13}C NMR are particularly efficient to locate and study the dynamics of surface ligands as well as to study hydrogenation and oxidation reactions. Surface reactivity of these nanoparticles will be presented both for solid / gas reactions such as CO and ethylene hydrogenation revealing some unexpected features such as the facile breaking of a C-C bond and for catalysis in solution, including asymmetric catalysis.

The presentation will detail first the surface reactivity of ruthenium nanoparticles and show in a second step how this knowledge can allow, in the case of iron, the growth nanoparticles of controlled size, shape and physical properties as well as that of iron carbide of tunable size.

INO-PL-03 Low Coordinated Phosphorus Compounds: Fictions, Facts, and Applications

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Rather exactly 50 years ago, H-C≡P - the phosphorus analogue of hydrogen cyanide - with a phosphorus carbon triple bond has been detected as a product in the decomposition of PH_3 in a plasma generated by a rotating arc struck between graphite electrodes. Since then, many unsaturated phosphorus compounds have been prepared by using bulky substituents in order to stabilize these highly reactive species kinetically. We have developed a straight forward access to unsaturated organophosphorus anions which is based on the reductive degradation of elemental phosphorus. Phosphaenolates, $R\text{-}P{=}C(OM)R^1$ (M = alkaline metal) play a crucial role as intermediates in the synthesis of phosphorus based photoinitiators produced on an industrial scale. A new simple synthesis of Na(O-C≡P) will be discussed which allows the synthesis of a wide range of functionalized organophosphorus derivatives.

INO-PL-04 Transition Metal Reaction Mechanisms via Density Functional Theory

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A focus on making and breaking of chemical bonds is what distinguishes Chemistry from other sciences. Thus, detailed knowledge of the mechanism of a chemical reaction provides a key to the understanding. Transition metals play an important role as catalysts in reactions that span the range from ethylene polymerization to enzymatic reactions.

This lecture will cover the background of modern computational chemistry especially density functional theory and illustrate its use with a number of examples, such as carbon-hydrogen bond activation, ethylene addition to nickel dithiolenes, conversion of azides to metal imidio complexes, alpha elimination on metal clusters, and protonation of diiron complexes related the hydrogenases, and C-X bond forming reactions supported by spin-state changes.

INO-PL-05 Molecular and nanosized catalysts for the conversion of renewables into energy and chemicals

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The simultaneous conversion of alcohols and sugars into energy and chemicals is a target of primary importance for the sustainable development. The realization of such a process provides renewable energy with no CO_2 emission and, at the same time, leads to the production of industrially relevant feedstocks, such as aldehydes, ketones and carboxylic acids. Such a target can be accomplished for a variety of renewable alcohols and carbohydrates, including ethanol, glycerol, ethylene glycol and sugars, by means of two electrochemical devices: *direct fuel cells* and *electrolyzers*. In either case, an aqueous solution of the fuel in the anode compartment is oxidized either on a nanostructured catalyst or on a molecular catalyst that are appropriately designed to promote selectively the partial oxidation of the anolyte with high stability and fast kinetics. When the oxidation process is carried out in a direct alcohol fuel cell (DAFC), the solid electrolyte is an anion-exchange membrane and electrical energy is released, while the alcohol is selectively converted to the corresponding carboxylic acid, isolated as alkali metal carboxylate (Figure 1) [1]. In an electrolyzer, containing an anode electrocatalyst similar to that employable in a DAFC, the electrolyte may be either an anion exchange-membrane or a solution of an alkali metal hydroxide (NaOH or KOH, for example) and the alcohol is converted to the corresponding alkali metal carboxylate, while hydrogen gas is produced at the cathode upon water reduction (Figure 1) [2].

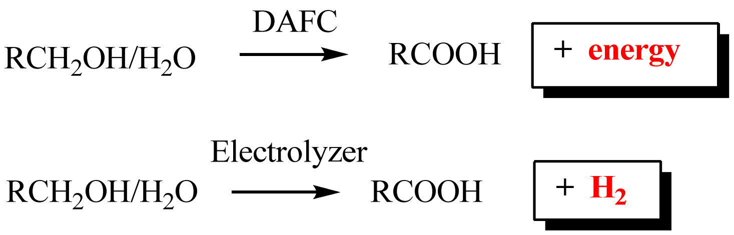

Figure 1.

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INO-PL-06 Photo-activation of TiO_2: insights from theory

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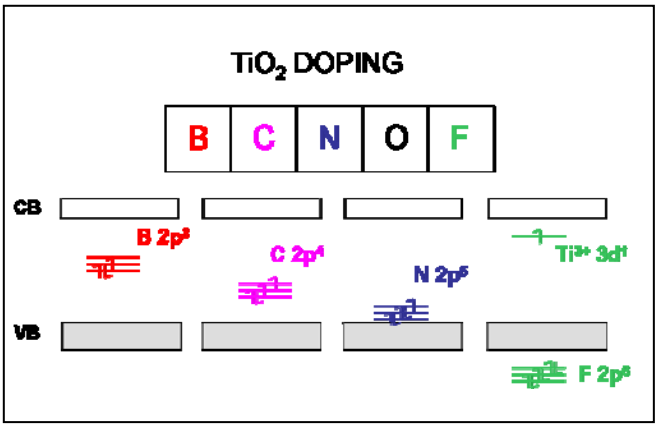
The theoretical approach nowadays has become an essential tool to address fundamental issues regarding inorganic chemistry and material science. Modern computational resources allow the calculation of very large models, thus removing the size limitation problem which in the past has prevented the study of realistic systems.

During the last few years we have applied density functional theory to improve the understanding of titanium dioxide material. TiO_2 is a versatile semiconductor used in several applications ranging from photocatalysis to self-cleaning coatings to solar cells, as a consequence of its ability to harvest solar light and convert it into other forms of energy or chemical reactivity. Most of the investigations are driven by potential applications, however, understanding of the underlying mechanisms is crucial for real progress in these fields.

Most of the times TiO_2 is doped or functionalized in order to lower the threshold energy for band gap electron-hole excitation in the vis-spectrum or to improve the surface photochemistry.[1]



The identification of the species formed and of their specific role is pivotal for improving the material performance. For example, doping with metal (such as Cr, Sb, and Nb)[2] or non-metal atoms (such as B, C, N, and F)[3,4,5] on one side introduces impurity states in the band gap reducing the absorption threshold of the material, on the other it may also cause the formation of oxygen vacancies or of Ti^{3+} species,[6,7] eventually relevant for the electron transport (n-type doping) and for the chemical reactivity at surfaces,[8,9] but also potential recombination centers.

In this lecture we will present an overview on recent findings related to doped, defective and photoexcited TiO_2 of special interest in photocatalysis and photochemistry. We will also show how the correct choice of the method is essential for the accurate description of the various species formed upon doping, functionalization and photoexcitation.

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INO-KN-01 Cell uptake and processing of metalated purines: a new possible path to antitumor and antiviral drugs

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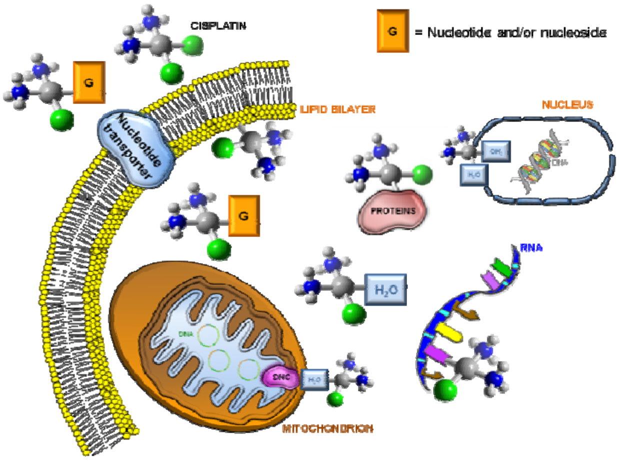
Cisplatin, *cis*-diamminedichloroplatinum(II), is one of the most widely used antitumor drugs in clinical therapy, as a critical component against a broad range of malignancies. Platinum anticancer compounds are known to target DNA where they can bind the *N7* of a purine base. *Cisplatin,* as other bifunctional agents, is also able to bind to adjacent G/A residues, resulting in the cross-link lesions believed to be responsible for the observed antitumor activity [1].

N7-metalated purines, in some cases, seem to be characterized by a relevant antitumor activity [2]. This has led us to hypothesize a *cisplatin* parallel mechanism of action: based on free platinated purines formation, directly in tissues, after drug administration, see Figure. In order to evaluate this possible mechanism as a key path to develop new drugs, we performed a series of experiments [3] focused on platinated nucleobases cell uptake and processing. In particular our researches were focused on the possible insertion of metalated nucleobases into nuclear and/or mitochondrial DNA/RNA synthesis, operated by DNA/RNA polymerases [4]. Model metalated nucleosides/nucleotides with nitrogen carrier ligands have been synthesized, isolated and characterized. For the first time cell uptake and mobility mechanism, related to plasmatic cell and/or mitochondrial membrane crossing, has been studied. The possible development of new drugs based on this new rational base will be discussed.



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INO-KN-02 Chemistry of Ni^{2+} in urease: sensing, trafficking and catalysis

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The biological essentiality of transition metals in enzymatic catalysis, coupled with their limited environmental availability, has driven organisms to evolve mechanisms for selective metal ion sensing and utilization. Changes in metal ions concentration are perceived by metal-dependent transcription factors, proteins that regulate the machineries of competitive metal ion homeostasis and metallo-enzyme activation. The intrinsic toxicity of the majority of metal ions demands a regulated intracellular trafficking, performed by specific chaperones. The Ni^{2+}-dependent urease enzymatic system is a paradigmatic case to study the strategies that cells use to handle an essential and yet toxic metal ion. Recent years have witnessed impressive achievements in the understanding of the biological chemistry of Ni^{2+} in the urease system.

The more recent advances in the comprehension of the specific role of Ni^{2+} in the catalysis and the interplay between Ni^{2+} and other metal ions such as Zn^{2+} and Fe^{2+} in the metal-dependent enzyme activity will be described, with special reference to the work carried out in our laboratory, tightly connected among, and strongly supported by, the partners the framework of CIRMMP (Consorzio Interuniversitario di Risonanze Magnetiche di Metallo-Proteine).

In particular, the structural features of the enzyme bound to inhibitors, substrate analogues and transition state or intermediate analogues have shed light on the catalytic mechanism. Structural and functional information has been correlated to understand the Ni^{2+} sensing effected by NikR, a nickel-dependent transcription factor. The urease activation process, involving insertion of Ni^{2+} into the urease active site, has been dissected and analyzed through the investigation of the molecular properties of the accessory proteins UreD, UreF and UreG. The Ni^{2+} intracellular trafficking has been rationalized through the knowledge of the structural and metal binding properties of the metallo-chaperone UreE. All the while, key general concepts have been revealed and developed, such as the overall ancillary role of Zn^{2+} in nickel metabolism, the intrinsically disordered nature of the GTPase responsible for coupling energy consumption to carbon dioxide requirement for the urease activation process, as well as the role of the accessory proteins regulating this GTPase activity. The overall activity of CIRMMP and its role in the development of this research will be illustrated.

INO-KN-03 A multidisciplinary research under the aegis of the INSTM consortium, exploration of the properties of nanostructured magnetic molecules

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INSTM is a consortium of 45 Italian Universities and groups about 2.000 researchers, post-docs and PhD students working in the area of Chemistry, Materials Science and Technology [1]. It is an original bottom-up aggregation of researchers, with a minimum of bureaucratic structure to efficiently coordinate activities and promote the joint participation of INSTM members to Italian and European projects. INSTM is also active in educational work, technology transfer, and establishing spin-off enterprises.

An example collaborative research coordinated by INSTM is represented by the joint efforts of the Firenze, Modena, Siena and Padova INSTM Research Units to investigate nano-assembling of magnetic molecules and its effects on the molecular properties [2-4]. The team also profited of an external collaboration with a French group through a European Network-of-Excellence project leaded by INSTM. Combining experimental methods like scanning probe microscopy, surface sensitive mass spectrometry and X-ray based spectroscopies with theoretical modelling it has been possible to demonstrate that certain molecules, known to behave as tiny magnets in the bulk phase, maintain their memory effect at the nanoscale, e.g. when assembled into a monolayer film on a metal surface [5,6]. These studies open the way to a strongly motivated research activity focused on the development of single-molecule based devices for spintronics.

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INO-KN-04 Catalysis: a Powerful Tool for Sustainable Chemistry

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There is a strong demand for more sustainable and environmentally benign synthetic methodologies suitable for the synthesis of chemicals and materials which are able to improve or maintain the current quality of life. Moreover an increasing ecological sensibility asks for renewable resources, alternative to fossil fuels, to produce synthons for fine chemicals, or polymers having the potential of biodegradation and/or biocompostation.

The UdRs of CIRCC are mainly active in the following five research lines of interest: *i)* New catalytic processes for industry, environment and energy; *ii)*Biomass for the production of energy and chemicals; *iii)* New environmental benign catalyst for the synthesis of polymeric materials from renewable resources; *iv)*Homogeneous catalysis and biocatalysis; *v)*Reactivity and modelling of organometallics and coordination inorganic compounds.

In this presentation some representative examples related to these topics will be provided. In particular the controlled synthesis of gold nanoparticles (AuNPs) of 4-9nm, incarcerated in a novel semicrystalline nanoporous polymer matrix will be described. This catalyst was successfully tested in the oxidation of primary and secondary alcohols using dioxygen as oxidant under mild conditions. The specific constant rates in the oxidation of (±)-1-phenylethanol to acetophenone and of benzyl alcohol to benzaldehyde are among the highest found for polymer incarcerated AuNPs. Similar values in terms of activity and selectivity were found in the oxidation of primary alcohols as cinnamyl alcohol and 2-thiophenemethanol, and secondary alcohols as indanol and α-tetralol. The catalytic properties were attributed to the formation of the nanoporous ε crystalline form of the polymer matrix that assures easy and selective accessibility of the substrates to the gold catalyst incarcerated in the polymer matrix. A comparison of the catalytic performances between the as synthesized and annealed AuNPs suggests that multiple twinned defective nanoparticle of about 9 nm are the active catalyst in these oxidation reactions. Some features of the reaction mechanism will be also discussed.

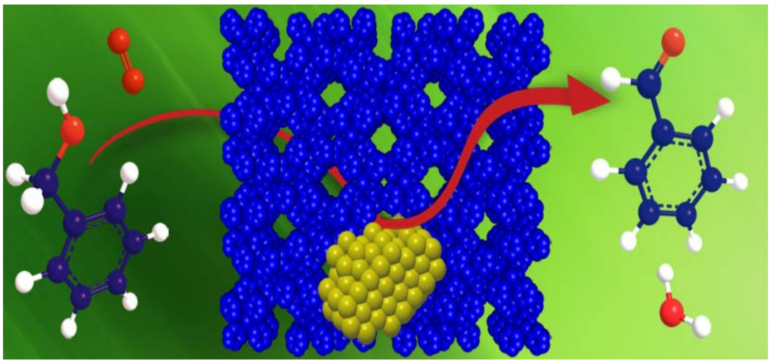

Figura 1. Selective oxidation of benzyl alcohol catalyzed by AuNPs incarcerated in a nanoporous polymer matrix.

INO-KN-05 Correlations between Structures and Chemical Behaviours

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X-ray diffraction, to determine geometries and stereochemical features of molecules, is still a fundamental tool to explore bonding and chemical reactivity. Small geometric differences between compounds and the variable 3D atomic arrangements provide much information on the chemical functionality. The structure-property relationships are based on electronic distributions, so that there are great expectations from the methods based on the electron density topology (QTAIM approach). However, even when they clearly detect bonding between two or more atoms, the underpinnings of the latter, the evolution of the associated chemical effects and their governing parameters may still present obscure points. The topological description of the wavefunctions provides more useful hints on the wider delocalization of the electrons, while perturbation theory concepts help to frame it intuitively. The remixing of the atomic orbitals, which follow a chemical substitution and/or a geometric rearrangement, is in fact rich of chemical information. Accordingly, combined structural and quantum mechanical strategies are often useful, by offering practical suggestions for even practical controls of the chemical behaviors.

An X-ray structure, as a snapshot of a molecule, already frames many chemical features and key aspects. Fortunately, the crystallographers have created, in a half century, a databank such as the Cambridge one, which contains more than a half million of catalogued structures. This should be immediately consulted for the classification of any new species. Moreover, the *horizontal* comparisons between strictly related molecules, with only minor differences, are a key to understand chemistry. Since a long time, our research has inspired to these criteria, which from the structural data address the essence of the bonding and reactivity. Selected cases will be pointed out based on the combination of crystallographic and QM (DFT and qualitative MO analysis) approaches. Our most recent work includes the very rare trigonal bipyramidal Pt_5 clusters, with the electronic stability unexpectedly provided by main group tin atoms [1]. In other cases, the comparative studies have pointed out questionable crystal structures in the databank, even though the X-ray technique is considered as most reliable and almost error-free. Sometimes, atoms of wrong nature have been assigned or the authors have overlooked some essential features [2]. Other examples will be illustrated of key X-ray structures, which have inspired a broader analysis of chemical reactivity or fluxional behaviors, In fact, given that DFT calculations properly mimic the observed compounds, it may be assumed that also the experimentally inaccessible optimized intermediates or transition states have to be regarded with the same confidence. This opens much wider horizons for the evolution of structures and their associated chemical relevance.

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INO-KN-06 Gaseous models of fundamental processes: the crucial role of ionic and neutral intermediates.

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According to a recent recommendation by Hoffmann et al., the thermodynamic and kinetic stability of a species is best described by the extreme concepts of "viable" and "fleeting" molecules [1]. Viable species have half-lives of a day or longer under ambient conditions, whereas fleeting molecules are local minima with barriers that prevent escape from their well. Charged and neutral fleeting species, though very short-lived, are important players in biochemical and atmospheric processes, as energy reservoirs, carriers of isotopic fractionation or intermediates of processes that convert complex starting materials (biomass feedstocks) into useful products [2]. As a consequence, the pivotal question is not "how long a molecule lives" but "the role it plays during its short life, and how strongly it affects other molecules' lives".

Mass-spectrometric approaches to the synthesis of *neutral* reactive intermediates have successfully discovered exotic, elusive species, proving their existence and kinetic persistence as intact, isolated species in the idealized gaseous phase [3]. These laboratory studies, performed under conditions similar to those existing in planetary atmospheres or in microenvironments in the absence of oxygen, pioneer the discover of new molecules in planets and interstellar clouds or help understanding biochemical processes relevant to cell regulation functions or modifications [2].

Useful models for more complex processes are also the ion-molecule reactions that lead to the activation and functionalization of hydrocarbons. Here the very nature of the *charged* intermediate may determine fast and efficient C-H activation steps, necessary to reach the goal of selective functionalization. The study of these gas-phase reactions has allowed the elucidation of the activation step mechanism, unraveling the crucial role played by the radical cationic character developped in intermediates and/or transition states. A significant contribution has been given by reactions that use metal-free electrophiles in the absence of catalyzers, like the radical cations SO_2^+ and $P_4O_{10}^+$ [4]. This has been recently suggested as a new possible route to the conversion of methane to more directly usable compounds [5]. Finally, the synthesis of isotopically specific intermediates proves to be a unique tool to investigate kinetic isotope effects in isotope-exchange reactions, suggesting a two-intermediates model for unconventional heavy-atoms kinetic isotope effects [6].

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INO-KN-07 Metalloprotein models: towards catalytic systems

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The predictive power of protein design methods has dramatically increased over the last years, with the challenge of preparing artificial models whose properties can mimic, enhance, and perhaps improve upon many features found in natural metalloenzymes [1].

To this aim, we designed catalytic artificial metalloproteins from α-helical coiled-coils, called DFs [2] and Mimochromes [3], whose active sites were engineered to reproduce the di-iron-oxo and heme-proteins functionalities, respectively.

Structural features of DFs and natural di-iron proteins, as well as functional elements of Mimochromes and natural horseradish peroxidase, were borrowed to obtain a *de novo* protein class with five-coordinated heme-complex and peroxidase activity, named MPs (Mini-Peroxidases). The basic structure of these models consists in a deuterohemin covalently linked to two *helix-loop-helix* peptide chains (Figure 1). The active site presents: (*i*) an *homo*-Cys/His residue in a single chain that acts as axial ligand to the iron ion,leaving the sixth coordination site able to accommodate exogenous ligands or substrates; (*ii*) an Arg residue in the distal site that should be able to activate hydrogen peroxide to give HRP-like catalytic process. The last analogue MP3 was successfully synthesized and characterized, and its biocatalytic efficiency was evaluated.

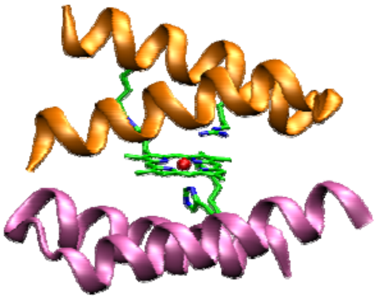

Figure 1

Results on the spectroscopic and structural characterization, together with functional implications, will be discussed.

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INO-OR-01 Metalloprotein mimics by design: strategies and applications

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Metalloproteins take part in a variety of life-sustaining processes and catalyze difficult reactions with efficiency and selectivity that few other natural or artificial molecules can achieve [1]. For this reason, structural and functional studies on metalloproteins have been the focus of many years of research. These studies require a simultaneous and accurate analysis of both the polypeptide chain and the metal cofactor herein embedded. In fact, the plethora of interactions that occur between the metal cofactor and the protein environment mutually affects the properties of each other, thus enhancing, diversifying or tuning their individual functions [2]. Understanding at a molecular level the mechanism by which the protein matrix finely tunes the environment of the metal cofactor is of fundamental importance in both basic and applied science.

Over the years, a large number of low molecular weight chemical catalysts has been developed as metalloenzyme mimics [1,2]. They have been basic in elucidating structure and function of metalloproteins and metalloenzymes; however they often fail in reproducing several features of biocatalysts, such as high turn-over number under mild conditions and high selectivity. Combining the advantages of chemical and biological catalysts would represent a daunting goal for chemists.

Tailoring synthetic models requires the development of sophisticated molecular architectures that distil the quintessential elements responsible for activities. Thus, peptide-based models seem valuable candidates to mimic both the structural features and reactivity of the natural systems. Using a structure-based strategy we have reproduced by design metalloprotein active sites. We centered our attention on iron-containing proteins, and we developed models for heme [3] and diiron-oxo [4] proteins. Our recent results on their structural and functional characterization will be presented. Their usefulness in biomedical and environmental applications, as well in biosensor construction, will be particularly highlighted.

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INO-OR-02 Molecular and Statistical Modeling of Physicochemical and Biological Properties of Antiproliferative Platinum(IV) Complexes

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Since the discovery of the antitumour activity of *cis*-$[PtCl_2(NH_3)_2]$, cisplatin, the search for alternative platinum complexes as antiproliferative agents has been an active area of research. Pt(IV) compounds represent an alternative class of potential prodrugs that are of considerable interest. These species are more inert to ligand substitution reactions than their Pt(II) counterparts, leading to lower systemic toxicity from unwanted side reactions and increasing the likelihood of the drug reaching its cellular target, the DNA. They are believed to be reduced in vivo to the active Pt(II) metabolite in the hypoxic, reducing and acidic tumor milieu. A judicious choice of the six ligands around Pt centre will modify the physicochemical properties of complexes (in particular lipophilicity and reduction potential) and, hence, their biological activity (bioavailability, cellular uptake, activation, and cytotoxicity). The ability to predict relevant physicochemical properties of Pt(IV) complexes directly from their structures would be an important step in rational design of new drugs, allowing potential candidates to be assessed before lengthy synthesis and testing.

We report the results of the quantitative structure-property relationship analysis of a series of Pt(IV) complexes. Molecular properties extracted from theoretical calculations [1] were used to construct models of experimental data such as electrochemical peak potentials (evaluated by cyclic voltammetry) and the octanol–water partition coefficient (evaluated by a RP-HPLC method). Statistically accurate models for both properties were found using combinations of surface areas, orbital energies, dipole moments, and atomic partial charges [2]. Moreover, theoretical and experimental descriptors were used to predict the antiproliferative activity of Pt(IV) complexes, directly from calculated data [3].

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INO-OR-03 What occurs replacing Mn^{2+} with Co^{2+} in Human Arginase I: a theoretical point of view

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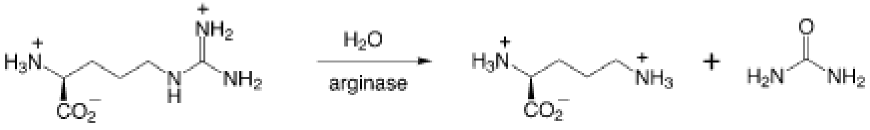
The human Arginase I (hArgI, EC 3.5.3.1) [1-2] is an enzyme containing usually two manganese ions (M_A and M_B) that generates a hydroxide to perform the nucleophilic attack on the guanidinium carbon of L-arginine, following the scheme:



l-ornithine urea

Recently, it has been reported that the incorporation of Co^{2+} in human arginase I (hArgI) shows a greater activity (k_{cat}/K_M) at pH 7.4 (close to the pH of human serum) while the native enzyme works at about 9.5 and has only fractional activity at physiological pH (~7.4). [3]
This behavior induced to consider the Co^{2+} substituted hArgI a promising new candidate for the treatment of L-Arg auxotrophic tumors. In fact, the Co-hArgI exhibits high cytotoxicity against human melanoma and hepatocellular carcinoma cell lines relative to that Mn-hArgI. [3]
With the aim to evaluate the influence of Co ion substitution to the native enzyme, the catalytic mechanism of the di-cobalt arginase has been investigated by using the density functional theory (DFT) employing different exchange-correlation potentials. Results are compared with that relative to the di-manganese native enzyme previously examined [4].

The University of Calabria and MIUR (Grant PRIN 2008F5A3AF_005) are gratefully acknowledged for financial support.

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INO-OR-04 Copper(II) coordination features of human angiogenin protein and related peptide fragments

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Human angiogenin (hAng) is a single-chain blood plasma protein present in physiological conditions, but over-expressed in patients affected by different types of cancers. Interestingly, the binding affinity between Ang and endothelial cells is largely increased in the presence of copper ions. It is well known that copper(II) is a strong angiogenic signal *in vivo*, but the specific molecular mechanism by which it works and the targets of its activity remain unclear. It has been demonstrated that extracellular translocation of the cellular copper occurs during angiogenesis processes, suggesting that the metal coordination by an extracellular protein involved in angiogenesis, such as angiogenin could be part of a signalling process. In this context, the characterization of copper(II) complex species with protein is a valuable aid in a better understanding of potential mutual biological influences. We report the coordination properties of peptide fragments encompassing the hAng N-terminal domain towards Cu^{2+} determined by means of combined potentiometric and spectroscopic techniques. The results obtained show that these fragments have an unusual copper binding ability. At physiological pH, the prevailing complex species formed by hAng(4-17) is [CuLH], in which the metal ion is bound to two imidazole and two deprotonated amide nitrogen atoms disposed in a planar arrangement. These complex species were used to probe the metal binding mode of the whole hAng protein and, at this aim, the recombinant hAng protein was expressed and a preliminary characterization of its copper(II) complexes was performed by means of EPR, CD and UV-vis measurements. The preliminary data indicate that the copper(II) complexes formed by the hAng protein, show a great similarity with those obtained for the N-terminal peptide fragments, suggesting that this domain may be the preferred copper(II) anchoring site in the whole protein. The high affinity for copper ion showed by the protein may give reasons of possible their interactions in vivo, and then of a potential correlation between copper and angiogenin.

INO-OR-05 Adaptive Chirality in Large Random Aggregates of Porphyrins

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Biomolecular structural motifs play a central role in the functioning of biological systems [1], and considerable effort has been focused recently on supramolecular interactions in the search for new probes capable of reporting on specific conformations of nucleic acids and proteins [2].

In the present study, poly-glutamate (PGA) has been chosen as model system to induce chiroptical properties on the aggregating metalloporphyrin trans-bis(N-methylpyridinium-4-yl)diphenylporphirinato copper(II) (t-CuPagg), and their interaction has been investigated through the combined use of UV/vis extinction, circular dichroism (CD), and Resonance Light Scattering (RLS) techniques.

We have previously examined the dependence of the porphyrin/protein interaction on protein concentration, ionic strength and pH, with particular focus on the effect exerted by the pH induced transition between PGA α-helix and random coil conformations [3]. Here, we report on very recent results[4] obtained on the interaction of preformed fractal aggregates of t-CuPagg with the same chiral scaffold. These point to an unprecedented mechanism of chirality induction that does not necessarily require the achiral monomers to self-organize in the presence of a chiral template, suggesting that a local distortion of the mesoscopic structure upon interaction with the asymmetric biopolymer might be sufficient to transfer the chiral information.

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INO-OR-06 Phenoxy-thioether group 3 and aluminium complexes as ε-caprolactone and lactide polymerization catalysts

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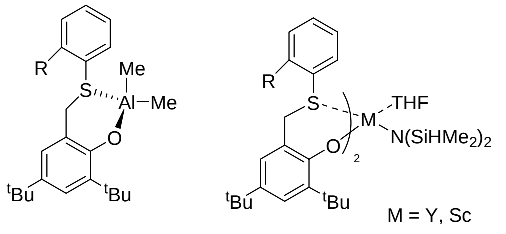
The interest in the synthesis of aliphatic polyesters stems mostly from their biodegrability, in relation to the recent concerns with the environments, and their biocompatibility which make them suitable materials for medical and pharmaceutical applications.

The ring opening polymerization (ROP) of cyclic esters via the coordination- nsertion mechanism enables the production of high molecular weight aliphatic polyesters with narrow polydispersities and well defined end groups. Among the wide range of metal compounds explored as catalysts for the ROP of cyclic esters, group 3 metal and aluminium species have been found well suited initiatiors.[1,2] While the former usual show a very high polymerization rate, the aluminium complexes generally lead to a lower activity but a better control over the polymerization process.



Ligand	R
1	H
2	Br
3	CH_3
4	CF_3

Figure 1

In this contribution we discuss the use of yttrium, scandium and aluminium complexes, bearing monoanionic bidentate phenoxy-thioether ligands, as initiatiors for the ROP of lactones and lactides. Four ligands with different substituents on the aromatic thioether ring have been synthesized and their effect on the catalytic behavior of the related complexes (Figure 1) has been evaluated. Several polymerization experiments, carried out by changing reaction conditions, such as solvent, temperature, etc., showed that, under certain optimized conditions, the ROP of the explored cyclic esters takes place in a living manner. Some caprolactone-lactide copolymerization experiments have been performed as well.

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INO-OR-07 Novel smart bio-materials: bioactive glasses containing metal nano-particles conjugated with molecules of biological interests

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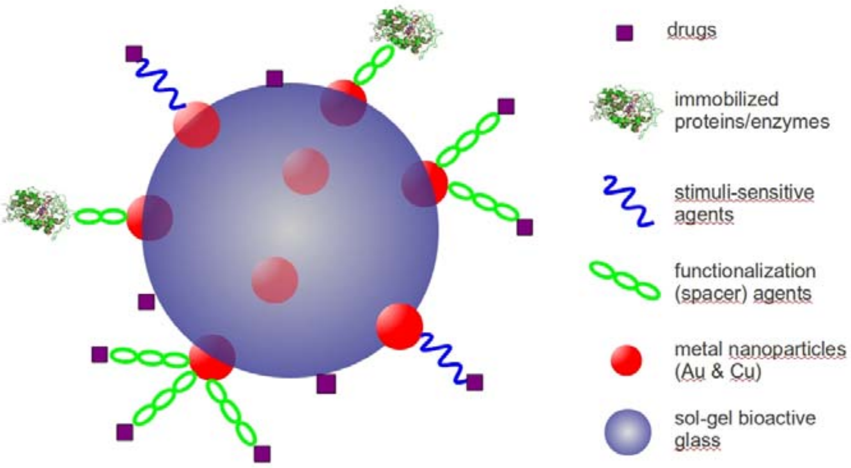
Stimuli-responsive materials (commonly referred to as *smart materials)* hold great promises for social and economic development and are of great relevance in both fundamental research and technological applications. Their design and realization through innovative processes involve complementary expertises, with comparable efforts on both synthetic and analytical sides. Within this work new *smart materials* based on phospho-silicate bioactive sol-gel glasses are been developed. To meet the ever-increasing demands for performing bio-materials, the surface features are been tailored to achieve optimal behaviour in different applications (*drug delivery, enzymes activity, chemo signalling probe, stimuli-sensitive agents*). In particular, the introduction onto the glass surface of metal nanoparticles (Au and Cu NPs) are very useful because the NPs can directly act, for example, as bactericides and imaging agents and can be used to immobilize, *via* a covalent linkage, an enzyme/protein and/or a drug on the glass surface through the formation of self-assembled monolayers (SAMs), in order to obtain a stable bio-conjugate systems. The materials prototyped in this way could be useful as a material bio-implantable into the human body. In this contribution we reported the last results of our works and some prospective in the field of smart bio-materials. [1-4]



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INO-OR-08 Reactivity and cell toxicity of surface modified TiO_2 nanopowders usable as sunscreen agents.

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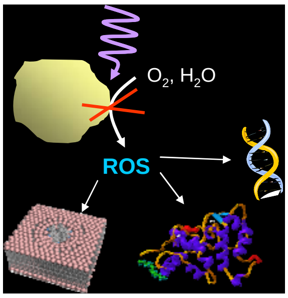
TiO_2 nanopowders are largely employed as UV-filters both in health care products and in polymeric composites. They found also applications in waste water remediation or as antibacterial agents. While in the latter case a good photocatalytic efficiency is needed when TiO_2 are used as UV-filters such activity needs to be suppressed since free radical species generated under sunlight exposure may cause both skin damage [1] and degradation of the organic components of the cosmetic preparations or composite.

In the last years a big effort has been made to increase the photocatalytic activity by the insertion of dopant elements in the structure [2] while a lower number of studies have been focussed on the reduction of the TiO_2 reactivity.

We have recently proposed a new modification of TiO_2 with carbon that reduces the photo-generation of free radical species maintaining unmodified its UV-filtering efficiency [3]. Here we explore a series of new modifications of the surface by using alcohols, carboxylic acids or iron salts. The modified powders have been characterized by TGA, EPR and IR spectroscopy. The oxidative potential of the powders in generating free radical species and the capability to cause damage to lipids, ribose or proteins has been evaluated by means of EPR spectroscopy/spin-trapping technique, UV/Vis spectrophotometry and SDS-page electrophoresis.



We found that the modifications performed largely reduce the oxidative potential of the TiO_2 powders. To investigate whether the observed modifications of photo-activity would affects the toxicological properties of the different TiO_2 powders the cytotoxicity and genotoxicity (oxidative damage) on human keratinocytes have been also evaluated.

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INO-OR-09 Gold and Silver Nanoparticles with Organic and Organometallic Thiols as Capping Agents

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Small metal particles can be used as functional units in innovative optoelectronic devices based on their quantum confined electronic properties. The synthesis and characterization of stabilized gold nanoparticles has been object of extended research studies, due to their enhanced optical properties [1] and cancer therapy applications [2]. Silver nanoparticles have also emerged in biomedicine studies [3]. The colloidal synthesis of organic and organometallic thiols stabilized Au and Ag nanoparticles has been achieved by using a two-phase synthesis. Among others, Pd(II) and Pt(II) containing organometallic thiol complexes [4] have been tested giving rise to nanostructures with controlled dimensions. The synthesis of gold nanoparticles (AuNP) stabilized by the bifunctional organometallic complex containing two Pt(II) centers, i.e. *trans, trans*-[$(CH_3COS)(PBu_3)_2Pt-C\equiv C-C_6H_4-C_6H_4-C\equiv C-Pt(PBu_3)_2(SCOCH_3)$], lead to the formation of dyads based on 4 nm nanoparticles. Water dispersible AuNPs and AgNPs capped by 3-mercapto propane sulfonate have been prepared in well defined and monodispersed structures with diameters in the range 2-4 nm; the dielectric behaviour of these materials has been studied to assess the electrical interfacial properties of metallic nanoparticles in aqueous solution [5].

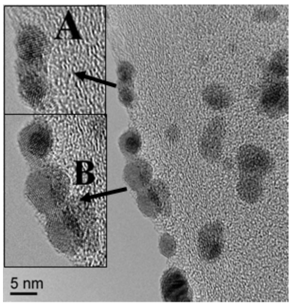

Fig. 1: HR- TEM of Pt(II) bifunctional organometallic thiol AuNP nanoparticles

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INO-OR-10 CuO-TiO$_2$ nanomaterials functionalized with Au nanoparticles: synthesis, characterization and gas sensing performances

Davide Barreca,[a] **Giorgio Carraro,**[b] **Elisabetta Comini,**[c] **Alberto Gasparotto,**[b] **Chiara Maccato,**[b] **Cinzia Sada,**[d] **Giorgio Sberveglieri,**[c] **Eugenio Tondello**[b]

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CuO-TiO$_2$-Au nanocomposites are appealing multi-functional materials for a broad range of applications, ranging from photocatalysis [1], to H$_2$ generation [2], up to solid state gas sensing. In this work, the above nanosystems were obtained by means of a hybrid vapor phase approach, consisting in: a) the Chemical Vapor Deposition (CVD) of CuO nanomaterials on Al$_2$O$_3$, starting from Cu(hfa)$_2$•TMEDA (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; TMEDA = *N,N,N',N'*-tetramethylethylenediamine); b) the CVD over-dispersion of TiO$_2$ nanoparticles (NPs) from Ti(dpm)$_2$(O-^{i}Pr)$_2$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate; O-^{i}Pr = isopropoxide) on the above matrices; c) the functionalization with gold NPs, performed through a mild sputtering process. The adopted strategy enabled to produce nanocomposites nanocomposites with tailored morphology, characterized by an intimate contact between TiO$_2$, Au and the hosting CuO matrices. Sensing tests for the detection of toxic/flammable gases, both reducing (H$_2$, CH$_3$CH$_2$OH) and oxidizing (O$_3$), evidenced that the simultaneous presence of TiO$_2$ and Au appreciably enhanced the overall performances. This effect highlighted the beneficial synergy arising from the high interfacial area *p*-*n* heterojunction between *p*-type CuO and *n*-type TiO$_2$, the Schottky-type barrier character of the gold-oxide interface, and the catalytic activity of TiO$_2$ and Au NPs. The high responses and low detection limits at moderate working temperatures are extremely promising for technological applications and evidenced the the importance of engineering oxide nanocomposites in order to design and master their functional performances.

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INO-OR-11 Perylene diimide – POSS dyes as a way to inhibit aggregation caused quenching

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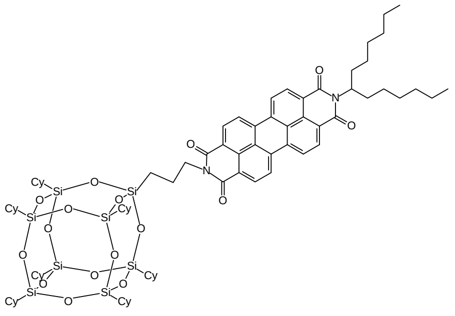
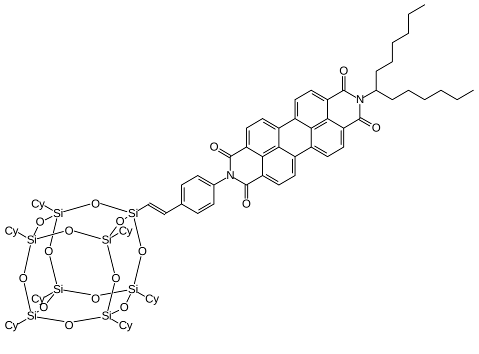
In recent years there has been an extensive research on the development of efficient solid-state emissive organic materials for organic optoelectronic devices, such as light-emitting diodes, organic field-effect transistors, solid-state lasers and fluorescent sensors. However, most organic chromophores are non-luminescent in the solid state, even if they are highly emissive in solution, owing to the quenching caused by intermolecular interactions such as aggregation caused by π–π stacking [1]. This is the case of perylene tetracarboxylic acid diimides (PDI), an important class of industrial pigments, which have been recently investigated for their interesting properties such as near-unity fluorescence quantum yields in solution, high photochemical stability, and strong electron-accepting character, that allow PDIs to be used in many electronic and optical applications [2].

We report on the preparation of PDI derivatives anchored to inorganic scaffolds such as Polyhedral Oligomeric Silsesquioxanes (POSS) with the aim to suppress the quenching which occurs in the solid state due to π–π stacking of this kind of emitting chromophores. The new PDI-POSS compounds here presented show in solution the typical absorption and emission features of the monomeric perylene unit, with a quantum efficiency close to unity, while in the solid state (both as spin-coated films and powders) the fluorescence quantum yield is positively affected by the presence of the POSS cage, with a quantum efficiency about 6 times that of the corresponding perylene tetracarboxylic bisimide in the solid state.





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INO-OR-12 Luminescent Silica Nanoparticles: Extending the Frontiers of Brightness

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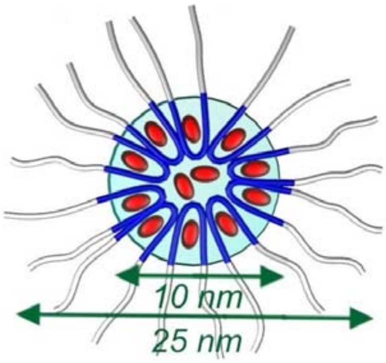
Silica nanoparticles are versatile platforms with many intrinsic features, including a low toxicity. Proper design and derivatization yield particularly stable colloids displaying multiple functions. In particular, a suitable choice of dyes and synthetic strategy yields very bright nanosystems, which can be used for either photoluminescence (PL) or electrochemiluminescence (ECL) sensing, labelling or imaging applications [1,2]. Silica nanoparticles thus offer unique potential in the nanotechnology arena, and further improvement and optimization could substantially increase their applications in fields of high impact, such as medical diagnostics and therapy, environmental and food analysis, and security.

This contribution describes silica-based multi-component nanosystems, tailored for optimization of processes such as directional energy- and electron-transfer, which provide those systems with extremely valuable functions: high light-harvesting capability, signal-to-noise maximization, multiplex output, signal amplification. A particular emphasis will be given to the description of a family of silica-core/PEG-shell nanoparticles, (see scheme 1) that we have recently developed in our laboratories.



Scheme 1: Cartoon of silica-core/PEG-shell nanoparticles as described in refs. 1-3

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INO-OR-13 Tracking thermally-activated transformations in a nanostructured metal/oxide/metal system

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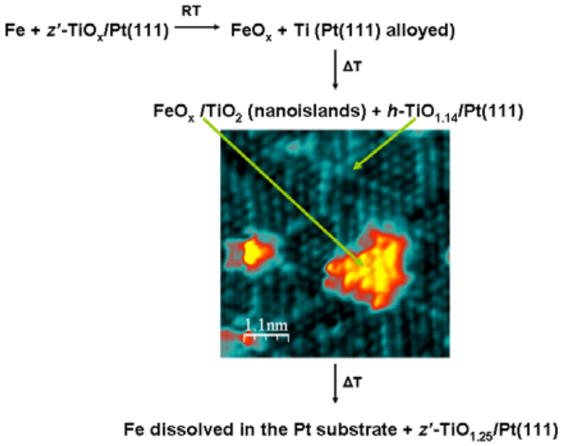
We present evidence of redox processes and structural transformations taking place in a Fe/z'-TiO_x/Pt(111) model catalyst in ultra-high-vacuum, studied by advanced surface science tools (photoemission, scanning tunneling microscopy and thermal programmed desorption) [1]. Competitive solid-state redox processes and chemical/structural transformations of both the Fe and FeO_x nanoparticle (NP) and the oxide ultrathin film take place as a function of temperature (see Figure below), giving rise to several distinctive phases at different temperatures. At RT the Fe and FeO_x NPs are templated by the ordered array of defects (troughs and picoholes) of the z'-TiO_x film, which is further reduced by Fe, partially forming a $PtTi_x$ surface alloy. At higher T (460<T<810 K), the system evolves to an intermediate state formed by a bi-component oxide material, i.e. mixed oxide FeO/TiO_2 nanoislands on a new hexagonal h-TiO_x ultrathin film, whose formation is triggered by the interdiffusion of Fe through the oxide into the Pt substrate. Eventually at higher temperature (>810 K) an almost complete migration of the Fe into the substrate is occurring and the pristine z'-TiO_x film formed again, demonstrating its intrinsic high stability.



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INO-OR-14 Reversibile Tuning of Light Emission Performances of Luminescent Metal-Tetrazolate Complexes

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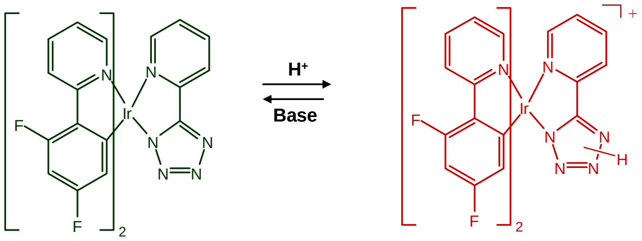
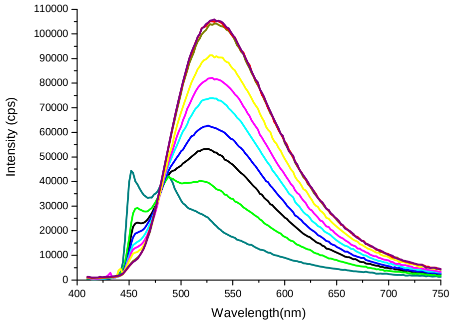
Over the past years, we have deeply explored the coordination chemistry of tetrazolates, $[R\text{-}CN_4]^-$. In particular, these derivatives proved as an excellent class of ligands for a variety of photo- and electroluminescent metal complexes such as Ru(II)-polypyridyls,[1,2], colour tunable Ir(III)-cyclometalates,[3,4] and, as the latest result, intensely emissive tris-carbonyl Re(I)-based compounds. [5] All of these complexes displayed a peculiar reactivity toward electrophilic species, which turns in the chance of performing both permanent and reversible modification of their structural features and, in particular, photophysical properties.





In this latter regard, the effects arising from the addition of CH_3^+ and H^+ to different types of tetrazolate complexes, will be described.

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INO-OR-15 Engineering copper phosphinates and bipyridines: sheets, ladders and (nano)tubes

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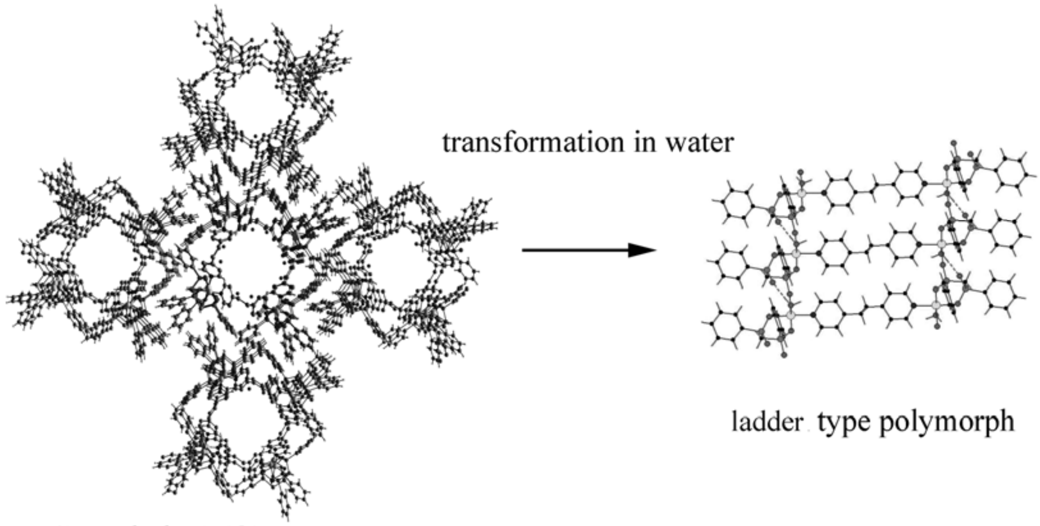
Tubular 1D-MOFs, built of discrete hybrid nanotubes assembled in the crystal packing and held together by Van der Waals interactions can be obtained by reaction of copper soluble salts with *pcp* and two ancillary N- ligands like *bipy* and *bipye* [(pcp = P,P' diphenyl-diphosphinate, bipy = bypiridine, bpye = 1,2-bis(4-pyridyl)ethane)]. The tubes have formula $[[Cu_2(pcp)_2bpye]\cdot2.5H_2O]_n$,**1** and $[[Cu_2(pcp)_2bipy]\cdot5H_2O]_n$, **2**. The exfoliation of the tubular MOFs **1** and **2** in organic solvents aided by ultrasonication allow to obtain elongated nanorods of variable size formed by the assembly of few single walled tubular shaped. An alternative synthetic route allows the synthesis of nanorods directly. The tubular 1D-MOFs show good and selective absorption properties towards polar solvents, like water and small alcohols, and gases such as CO_2.While **2** is the only isomer that could be obtain, an interesting spontaneous phase transformation in water of tube **1** leads to the formation of pseudo polymorphic ladder type structure of formula $[Cu_2(pcp)_2bpye(H_2O)_2]_n$ (**1a**) . On the contrary the use of a longer bypridine, namely *bipyp* 1,2-bis(4-pyridyl)propane), leads to a mixture of two different closely packed compounds with formula $[[Cu_2(pcp)_2bipyp(H_2O)]H_2O]_n$ (**3**) and $[[Cu_2(pcp)_2bipyp]\ 2H_2O]_n$ (**4**). Some considerations on how supramolecular forces are involved in the building of the three-dimensional structures in the solid state, will be discuss.



INO-OR-16 Synthesis and characterisation of Cu-Sn-Zn-S photovoltaic materials.

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Photovoltaic devices based on related sulfoselenide compounds show interesting properties, suggesting their possible application in the field of solar cells. In particular the Cu_2ZnSnS_4 (CZTS, kesterite) compound is a promising thin film photovoltaic absorber material and the kinetics of film growth of the Cu-Zn-Sn-S system was investigated by different research groups. Olekseyuk et al. [1] have found that Cu_2ZnSnS_4 melts incongruently at 1253K, crystallizing by peritectic reaction with a composition of the liquid phase far poor in ZnS. As a consequence the crystal growth from the melt, besides the Cu_2ZnSnS_4, results in the presence of impurity phases such as Cu_2SnS_3, ZnS and SnS [2]. The solidification of a CZTS single-phase from the stoichiometric melt might be improved by the presence of a suitable seed or the action of a directional cooling, like in the Czochralski or the Bridgman-Stockbarger techniques [3].

Although many studies have been performed on CZTS thin film, information on the bulk material, such as formation and stability of intermediate phases, extension of the compositional homogeneity range and crystal structures can be very important. Indeed, this has been the subject of recent studies by Muska et al. [4] on monograin powders synthesized via the molten flux technique. During our research, two methods have been used for the synthesis of the Cu_2ZnSnS_4. Single crystals have been produced within sealed quartz ampoules via the Chemical Vapour Transport technique using I_2 as the transporting agent; the effects of temperature gradient and I_2 load on the crystal habit and composition have been considered. Bulk samples have been produced using a solid state reaction method starting from mixed and compressed powders of the elements enclosed in a quartz tube under vacuum for heat treatments. The synthesized samples have been observed using a Scanning Electron Microscope equipped with an Energy Dispersive X-ray Spectrometer. The results obtained will be presented and discussed.

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INO-OR-17 1D and 2D ^{31}P NMR spectroscopy as diagnostic tool to assess chemical exchange around P_4 moieties.

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A surprising "*planetary*" exchange mechanism around the tetraphosphorus cage in complexes [Ru(H)(P-P)$_2$(η^1-P$_4$)], (P-P = $Ph_2PCH_2PPh_2$, dppm, **1**; $Ph_2PC_2H_4PPh_2$, dppe, **2**) was demonstrated by solution NMR experiments and DFT calculations. Further activation of Ru(dppm)$_2$-coordinated P$_4$ by a Pt(0) carbene-like fragment gave a bimetallic ruthenium/platinum complex showing instead an intriguing "*pendulum-like*" fluxional behaviour in solution[1]. The presence of a ligand with larger bite-angle, *dppe*, seems to be responsible of a new planetary motion involving the $[RuH(dppe)_2]^+$ and $Pt(PPh_3)_2^{2+}$ fragments. Finally, a comparison between the dynamic behavior of **1** and **2** and other η^1-P$_4$ derivatives such as $[CpM(PPh_3)_2(\eta^1\text{-}P_4)]^+$ (M = Ru, Os) will be shown.[2]

Herein we show that 2D ^{31}P EXSY experiments can be used as qualitative tools to unravel the nature of dynamic processes of transition metal-(η^1-P$_4$) complexes and their platinum adducts. Rate constants were extracted using DNMR Lineshape analysis of 1D Variable-Temperature ^{31}P{^{1}H} NMR spectra.

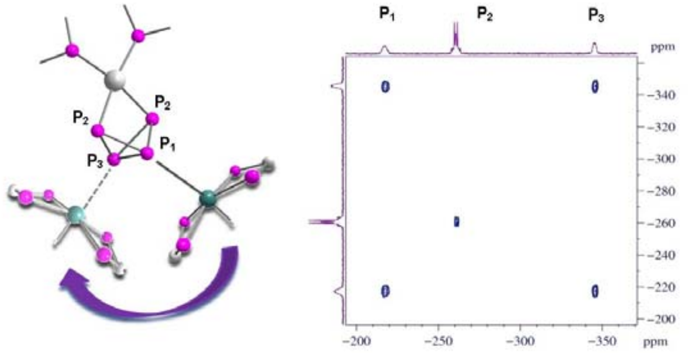

Figura 2. Pendulum motion: ^{31}P EXSY recorded at -25°C, τ_m = 100ms

COST Action CM0802 «PhoSciNet» is kindly acknowledged for support. Thermphos Int. B. V. is thanked for a generous loan of white phosphorus.

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INO-OR-18 Dicationic μ-diborolyl triple-decker complexes [CpCo(μ-1,3-$C_3B_2Me_5$)M(arene)]$^{2+}$ (M = Rh, Ir). Synthesis, Structure, and Electrochemistry

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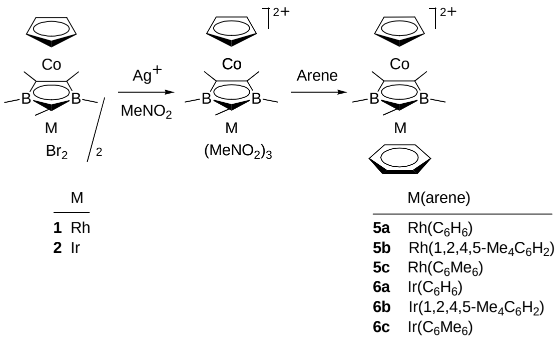
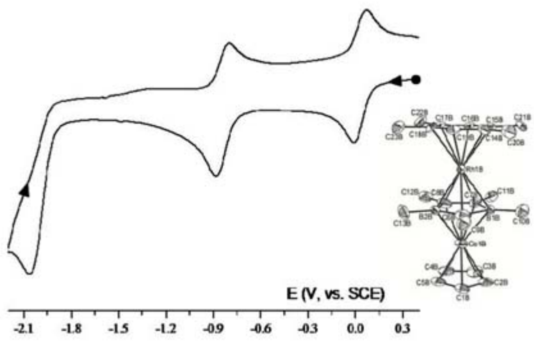


Reaction of the bromide complexes [CpCo(μ-$C_3B_2Me_5$)MBr_2]$_2$ (M = Rh, **1**; Ir, **2**) with $AgBF_4$ in acetonitrile solution affords the dicationic tris-(acetonitrile)μ-diborolyl triple-decker complexes [CpCo(μ-1,3-$C_3B\,Me_5$)- M(MeCN)$_3$]$^{2+}$ (Rh, **3**; Ir, **4**).

The labile nitromethane solvates [CpCo(μ-1,3-$C_3B_2Me_5$)M($MeNO_2$)$_3$]$^{2+}$, generated in a similar way, react with benzene and its methyl derivatives affording the arene triple-decker complexes [CpCo(μ-1,3-$C_3B_2Me_5$)M(arene)]$^{2+}$ (M = Rh, **5**; Ir, **6**; arene = C_6H_6 (**a**), 1,2,4,5-$Me_4C_6H_2$ (**b**), C_6Me_6 (**c**)). Crystal structures of **5b**(BF_4)$_2$, **5c**(BF_4)$_2$ and **6b**(BF_4)$_2$ have been determined by X-ray diffraction.

In propylene carbonate solution, complexes **5a-c** and **6a-c** undergo two chemically and electrochemically reversible reductions, followed by further irreversible processes. Representatively, Figure 1 shows the cyclic voltammetric response of **5b**. Controlled potential coulometry proved that the first cathodic process involves one electron/molecule.



Methyl substituents play an important role on the location of the redox potentials, in that, as expected, the increase of their number makes the reduction more and more difficult.

Details on structure, electrochemistry and spectroelectrochemistry will be discussed.

INO-OR-19 ACTIVATION OF CARBOPLATIN BY CARBONATE: A THEORETICAL INVESTIGATION

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Carboplatin, cis-diammine(cyclo-butane-1,1-dicarboxylato)-platinum(II), is a second-generation cisplatin analogue with reduced toxicity, widely used in the clinical treatment of cancer and most active against testicular and ovarian tumors.[1] While the cisplatin aquation kinetics is fast enough to allow the drug to react with water and biological components under physiological conditions, the much slower substitution rate of carboplatin likely precludes hydrolysis as a means of activating the drug in vivo, and several suggestions have been made to account for its activity in vivo, focusing on potential ligands for the Pt(II) center present in the blood plasma.[1] Among them, the carbonate ion, which is present in high concentration in the blood plasma, was suggested to play a potential role in the activation of platinum-based anticancer complexes.[2]

We carried out a theoretical study on the thermodynamics and the kinetics of the activation of the anticancer drug carboplatin in carbonate buffer, a process which has been suggested to play an important role in the uptake, antitumor activity and toxicity of this drug. The initial stages of this process have been investigated by considering the bicarbonate ion, the most abundant species at physiological pH, as the attacking species and consist of an initial ring-opening step, involving the displacement of one arm of the chelating ring by the bicarbonate ion, followed by the decarboxylation of the ring-opened species to give the corresponding hydroxo product. The obtained results show that the overall process is essentially thermoneutral with relatively low activation enthalpies for the two considered steps (122.5 and 91.9 kJ mol^{-1}, respectively) suggesting that the reaction with bicarbonate might represent a viable pathway for the activation of carboplatin to give active intermediates which, in the biological environment, may easily further react to give thermodynamically more stable species.

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INO-OR-20 PROTONATION OF A PHOSPHINITO BRIDGED DIPLATINUM(I) COMPLEX CARRIED OUT WITH "CLASSIC" (HBF_4) AND UNUSUAL (HF) BRØNSTED ACIDS

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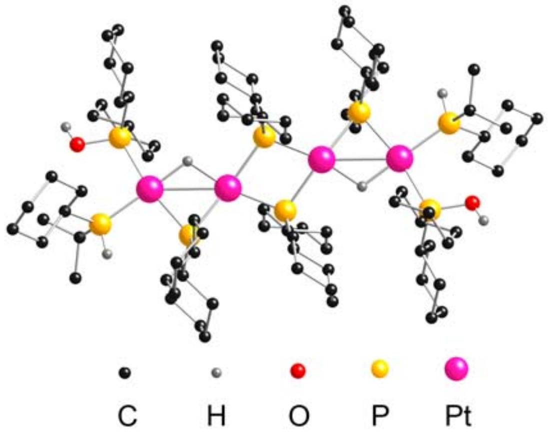
The phosphinito bridge of the complex $[(PHCy_2)Pt^1(\mu\text{-}PCy_2)\{\kappa^2P,O\text{-}\mu\text{-}P(O)Cy_2\}Pt^2(PHCy_2)]$ (*Pt-Pt*)[1] (**1**), differentiates the charge distributions on the two platinum atoms and renders the Pt-O fragment the reaction core of the molecule in reactions with nucleophiles[2] electrophiles,[3] or small molecules such as H_2.4 This presentation deals with the products and the mechanisms of the reaction of complex **1** with Bronsted acids having poorly coordinating anions such as HBF_4 and HF.[5] A comparison will be made between results obtained with HBF_4 and those obtained with HCl and HI. The unexpeted product obtained with diluted HF is depicted below.



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INO-OR-21 Surface Decorated Platinum Carbonyl Clusters

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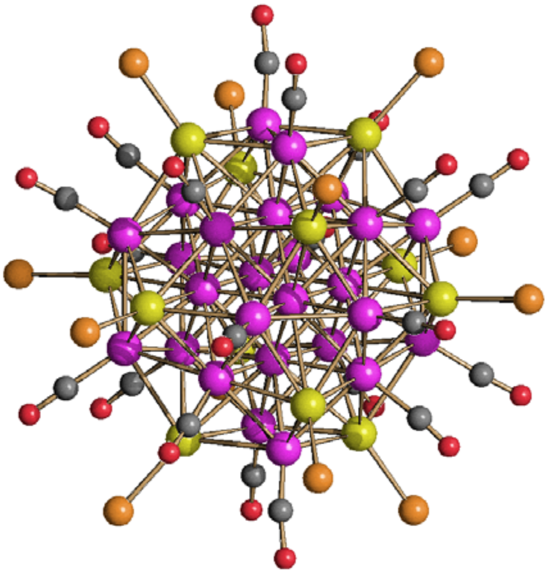
Since the discovery of the so called “platinum carbonyl”, $[Pt_{3n}(CO)_{6n}]^{2-}$ (n ~ 10), platinum has played a key role in the development of molecular cluster chemistry.[1] Nonetheless, the number of species completely characterised is rather limited. Aiming at extending this chemistry, we have recently investigated the reactions of platinum Chini clusters, $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2-8), with miscellaneous Cd(II) salts and phosphines.[2] This led to the isolation and crystallographic characterisation of new species such as $[Pt_{13}(CO)_{12}\{Cd_5(\mu\text{-}Br)_5Br_2(dmf)_3\}_2]^{2-}$, $[Pt_{19}(CO)_{17}\{Cd_5(\mu\text{-}Br)_5Br_3(Me_2CO)_2\}\{Cd_5(\mu\text{-}Br)_5Br(Me_2CO)_4\}]^{2-}$, $[Pt_{26}(CO)_{20}(CdBr)_{12}]^{8-}$ (Figure) and $[Pt_{22}(CO)_{22}(PPh_3)_6]^{2-}$, which are herein presented.



All these clusters are composed by a Pt-CO core decorated by various Cd(II) or Pt-PR$_3$ based fragments. These surface decorations may be related to that of Au-Fe-CO clusters, *e.g.* $[Au_{21}Fe_{10}(CO)_{40}]^{5-}$,[3] as well as to the staple motifs stabilizing gold thiolates nanoclusters, *e.g.* Au$_{102}$(S-p-benzoic)$_{44}$.[4] An oversimplified and unifying approach to interpret the electron counts in all these species is suggested, indicating that molecular metal cluster chemistry may give fundamental contributions to the understanding of some facets of nanochemistry and may provide a reliable guideline to interpret ligand-stabilized metal nanoparticles.

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INO-OR-22 Probing the role of related ring substituents over the electronic structure of ferrocene *via* synchrotron radiation photoabsorption and photoemission

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In the last years, substituted ferrocenes have been investigated as active redox molecules, able to tune the response of a functionalized electrode (especially gold and silicon) on which they are adsorbed, due to their attractive electrochemical characteristics: fast electron-transfer rate, low oxidation potential, and two stable redox states [1]. Ferrocene derivatives present also the advantage of a facile tunability of their redox potential via substitution of one or more H atoms of the cyclopentadyenil (Cp) ring with distinct functional groups. [2,3]

We present the results of an experimental and theoretical investigation on pure ethyl-, vinyl- and ethynylferrocene in the gas phase by means of NEXAFS at the C K-edge, and XPS of the C 1s region, and by DFT calculations.[4] Such a combination probes both the state of charge of the C atoms of the substituent group of the three molecules, and the extent of conjugation of the C-C arm with the Cp ring. A reliable assignment of the characteristic NEXAFS features associated to double and triple C-C bond of the lateral substituents of such closely related molecules may offer the fingerprint of the preservation or loss of the unsaturation in the anchoring arm upon its reaction with a surface, as well as shed light on the reaction mechanism for the surface anchoring on Si with different recipes, which is an actively investigated, yet still open, issue.[5]

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INO-OR-23 Effect of nonsymmetric N-donor ligands in Pd-catalyzed alkene/acrylic ester copolymerization

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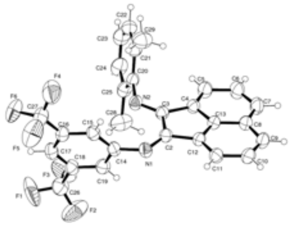
One of the major unsolved problems in the field of polymer chemistry is represented by the synthesis of copolymers of alkenes with polar vinyl monomers [1]. Single-site metal catalyzed polymerization is potentially the most powerful, environmentally-benign method for the controlled synthesis of new polymeric materials. For the target reaction, the most promising catalytic systems are based on late transition metals, in particular palladium. Two major types of catalysts have been reported: Pd complexes based on α-diimines [2]; Pd-phosphino-sulphonate derivatives [3].

We have now studied two new nonsymmetric α-diimine ligands (Ar,Ar'-BIAN) featured by one aryl ring substituted in *ortho* positions with electron-donating groups and the other ring with electron-withdrawing groups on the *meta* positions (Figure). The catalytic behavior of the relevant Pd-complexes [Pd(CH_3)(Ar,Ar'-BIAN)(L)][PF_6] (L = CH_3CN, dmso) in the alkene/methyl acrylate copolymerization has been studied in comparison with that of the complexes containing the corresponding symmetric α-diimines. The studied alkenes are ethylene and 1-hexene. Alkene/methyl acrylate oligomers are the products of the catalytic reaction.



It was found that the catalysts containing the Ar,Ar'-BIAN ligands show a higher productivity and a higher content of the incorporated polar monomer than the active species with the symmetric α-diimines. The distribution of the polar monomer into the oligomer is also different from that reported in the literature [2].

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INO-OR-24 Nb(V) and Ta(V) Haloanions as Effective Counterions for the Room Temperature Isolation of Salts of Uncommon Organic Cations

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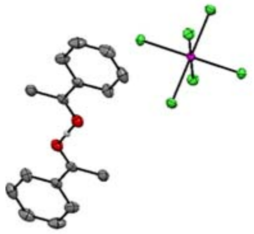
In the framework of our recent studies on the direct interaction of MX_5 (M = Nb, Ta; X = F, Cl, Br) with oxygen compounds, we have been aware that M(V) haloanions possess outstanding capability of stabilizing uncommon organic cations. Reactions involving ketones or polyethers may be accompanied by C−H bond activation, thus the salts $[(MePhCO)_2(\mu\text{-}H)][TaCl_6]$, **1** (Fig. A) [1], and $[diglyme(H)][NbCl_6]$, **2** [2], have been isolated in the respective cases. Otherwise the reaction of $NbCl_5$ with $CMe_2(OMe)_2$ proceeds with C−O cleavage and leads to selective formation of the methylated mesityl oxide species $[Me_2C{=}CHC({=}OMe)Me][NbCl_5(OMe)]$, **3** (Fig. B) [3]. A series of $[Nb_2F_{11}]$ radical cation salts of monocyclic arenes have been prepared according to unexpected redox reaction including metal reduction [4]. These salts are surprisingly long-lived at room-temperature or above, due to stabilizing cation-anion interactions; the $[C_6H_6]^+$ radical has been identified for the first time by EPR as a *non-transient species* in solution at room temperature. The same redox pathway has been exploited for the straightforward synthesis of thermally stable $[M_2F_{11}]^-$ salts of protonated 1,3-dimethoxybenzene (Fig. C) [5].



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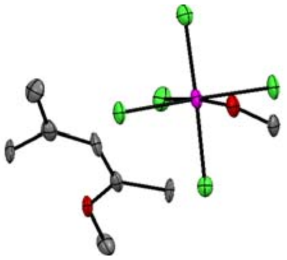

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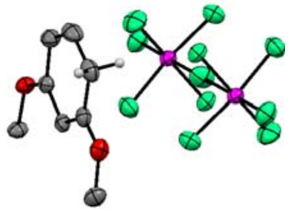

C

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INO-OR-25 Metal complexes with dendritic ligands

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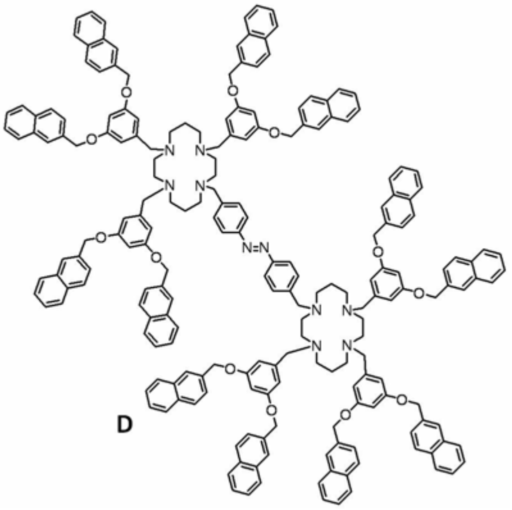
Dendrimers[1] are highly branched tree-like macromolecules with well-defined composition and a high degree of order. They usually consist of a core upon which radially branched layers are covalently attached. By using suitable synthetic strategies it is possible to prepare dendrimers that contain selected functional units in predetermined sites of their structure. Such compounds can often exhibit remarkable chemical, physical and biological properties, with a wide range of potential applications in different fields such as medicine, biology, chemistry, physics, and engineering.



In the last few years, we have investigated several families of dendrimers containing a 1,4,8,11-tetraazacyclotetradecane (cyclam) core, one of the most extensively investigated ligands in coordination chemistry, to build up metal complexes with dendritic ligands.[2] Particularly interesting results have been obtained in the case of dendrimer **D** (see figure). It is constituted by two cyclam units linked by a photoswitchable azobenzene chromophore and 12 naphthalene units at the periphery. In this dendrimer, the distance between the two cyclam units can be modulated by light stimuli thanks to the presence of an azobenzene moiety which can be reversibly switched between trans and cis isomer by light irradiation. Therefore, the trans and cis isomers display different coordination ability toward Zn(II) ion in $CH_3CN:CH_2Cl_2$ solution. Moreover, upon naphthalene excitation photosensitized azobenzene isomerization takes place.

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INO-OR-26 From covalent to supramolecular wheel-and-axle metallorganic crystalline materials for gas-uptake processes

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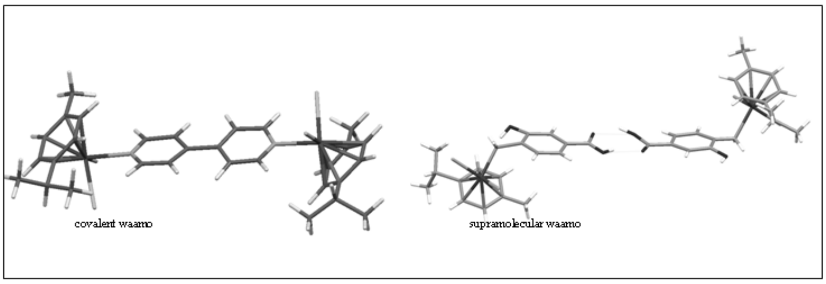
In the last decades much effort has been expended to the development of crystalline materials able of incorporating small molecules into the lattice through weak interactions [1]. These materials appear appealing in different strategic fields such as catalysis, development of chemical sensors as well as gas storage devices. Their inclusion propensities strongly depend on the shape and size of the molecular building blocks chosen for fabricating the crystalline scaffolds. In the last years we have focussed our attention on the development of organometallic complexes with a wheel-and-axle (WAA) morphology, which are constituted by two bulky groups (wheels) connected by a central linear spacer (axle) [2]. In the titled complexes, the wheels are represented by half-sandwich ruthenium(II) units, while the central axle can belong to two different classes: *class I*, covalent axles; *class II*, supramolecular axles. For the construction of WAA compounds belonging to *class I* it is necessary to use divergent rigid bidentate ligands, such as 4,4'-bipiridyl, 4-cyanopyridine, trans-1,2-bis(4-pyridyl)ethylene or 4,4'-bis-(diphenylphosphine)biphenyl, while for WAAs belonging to *class II* the employed ligands must contain organic functions able to give rise to supramolecular linear synthons, such as 4-aminobenzoic acids or the corresponding amides, through the COOH and $C(O)NH_2$ functions.

In this communication an overview of the WAA-metallorganic systems (WAAMO) developed in our laboratory belonging to classes I and II will be shown, together with some case studies of their propensity to capture volatile organic molecules through heterogeneous gas-uptake experiments.



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INO-OR-27 New europium (III) chiral complexes: Spectroscopy and molecular structure in the solid state

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Luminescent lanthanide complexes have interesting photophysical properties mainly due to the spectroscopic features of the metal ion. Although Ln(III) ions have weak absorption intensities, due to the Laporte forbidden nature of the intraconfigurational f-f transitions, this disadvantage can be overcome by indirect sensitization through the absorption bands of the ligand molecules coordinated to the Ln(III) ion using UV light (antenna effect). Concerning the applications in the biomedical field, Eu(III) complexes exhibit some desirable and unusual characteristics when compared with conventional organic fluorophores such as long excited-state lifetime (in the ms-range), large shift between absorbed and emitted wavelength and narrow emission bands both allowing the separation between Ln(III) luminescence and short-lived background fluorescence [1]. Recently, the interest in Ln(III) compounds possessing chiral properties has started to increase due to new chiral sensing/recognition applications [2, 3]. In the present contribution we studied the relationship between the luminescence properties of Eu(III) ion and the solid state molecular structure of the complexes depicted in Fig.1. The results of this study and some preliminary evidences in solution reveal that this new family of Eu(III) complexes are promising candidates for applications in the sensing field as probes in solution of the nitrate anion and of chiral molecules.

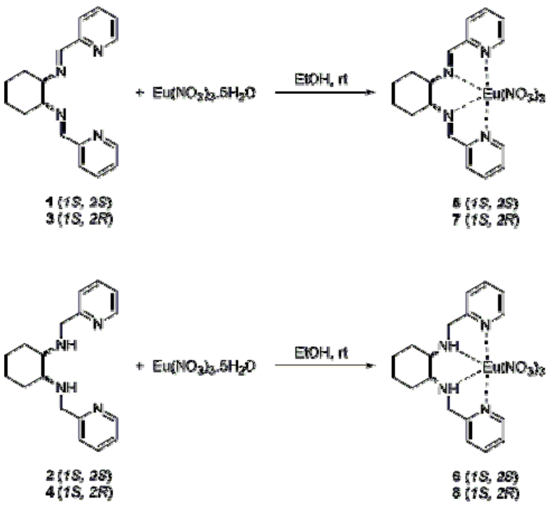

Figure 1

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INO-OR-28 ENANTIOSELECTIVE CYCLOPROPANATION REACTIONS CATALYZED BY CU(I) COMPLEXES OF PYRIDINE CONTAINING MACROCYCLIC CHIRAL LIGANDS (PC-L*) SUPPORTED ON SILICAS.

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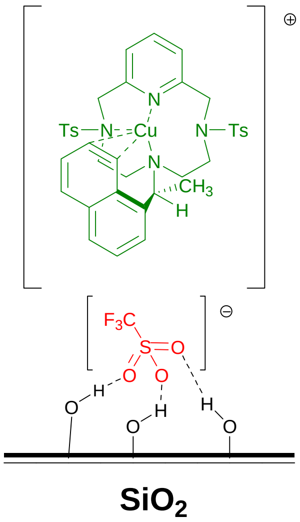
We have reported that copper(I) complexes of the new C_1-symmetric pyridine-based 12 membered tetraaza macrocyclic (**Pc-L***) ligands are competent catalysts in the enantioselective cyclopropanation of olefins employing ethyl diazoacetate (EDA) as carbene precursor in homogeneous phase[1]. Heterogeneous single site catalysts in many cases show superior performances in terms of activity, selectivity and recyclability coupling together the advantages of heterogeneous and homogeneous systems [2]. Aim of the present work has been to heterogeneize the chiral copper(I) complexes on mesoporous silicas and to test them as catalysts in asymmetric synthesis.

Pc-L* Cu(I) complexes were grafted on mesoporous ordered and non-ordered silicas (MCM-41, SBA-15 and Davisil) by the SHB method (Figure).[2] SHB (Supported by Hydrogen Bond) is a simple, very mild, rather strong grafting, procedure applicable to a wide range of metal complexes bearing the SO_3^- moiety as counterion.

Materials obtained were fully characterized for metal content, textural properties, hydrogen bonds between Cu(I) complex and surface silanols by a variety of techniques. Catalysts were tested in enantioselective cyclopropanation reactions of olefins. The results will be presented in terms of chemical yields and stereochemical outcome and compared with those obtained in homogeneous phase. The confinement effects, namely the pore size influence as well as the issue of catalyst separation and recyclability were studied and rationalized.



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INO/OM-KN-01 Metal-coordinated carbenes: reactive species or robust ligands?

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Transition metal carbene complexes have been mainly considered reactive intermediates in several catalytic organic transformations, like for example, the reactions involving the decomposition of diazo compounds (cyclopropanations, C-H insertions, C-C coupling) [1].
However, since the discovery of stable imidazol-2-ylidenes, which were first isolated by Arduengo *et al.* in 1991, much interest has been growing in the chemistry of N-heterocyclic carbenes (NHCs) [2]; in fact, these resulted to be excellent ligands towards transition metal centres both in low and medium-high oxidation state, allowing the synthesis of robust catalysts with negligible carbene dissociation, stable in acidic and oxidative environment.
The dual nature of carbenes can be illustrated by selected examples taken from our recent results involving:
A) reactions of reactive carbene intermediates such as i) insertion of carbenes into C=C, C-H and O-H bonds catalysed by Pt(II) and Rh(II) complexes; ii) reaction of diazo derivatives in presence of olefins to give metathesis and cyclopropanation products catalysed by [RuCl(Cp)(COD)] [3];
B) synthesis of novel di- and tricarbene Pd(II), Pt(II), Cu(I), Ag(I), Au(III) complexes and applications as catalysts in i) Heck reaction, ii) selective hydroarylation of olefins, iii) Ullmann-type arylation [4].
The obtained results show the extraordinary flexibility of the carbene mojety and fully justifies the strong research efforts on this still new and fascinating chemistry.

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INO/OM-KN-02 Stereoselective Gold Catalysis: New Opportunities in Organic Synthesis

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The re-discovery of homogeneous gold(I) catalysis has recently revolutionized the whole organic synthesis scenario, opening up access to unprecedented synthetic manipulations of unfunctionalized unsaturated hydrocarbons under mild and environmental acceptable conditions.[1] At the same time, new opportunities were also created in the "crowded" area of asymmetric catalysis, providing reliable solutions to the preparation of enantiomerically enriched polyfunctionalized molecular architectures in the presence of chiral gold(I) complexes.[2]

In conjunction with our ongoing interests oriented to the catalytic enantioselective decoration of arenes,[3] we have recently reported on the effective gold-mediated direct electrophilic activation of allylic alcohols,[4] in the preparation of functionalized heterocyclic compounds (*i.e. morpholines, indolines, carbazoles*).[5] This consolidated background, along with the use of propargylic alcohols in gold-catalyzed cascade cyclization reactions[6] concur to define new guidelines in organometallic synthesis under noble metal assistance.

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INO/OM-OR-01 Pd/Ln_xO_y (Ln = La, Ce, Pr, Sm, Gd, Dy and Yb): Efficient Precatalysts for a Fast and Green Suzuki-Miyaura Reaction

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In the last two decades, the Pd-catalyzed C-C bond formation has emerged as an outstanding strategy for building more or less complex organic molecules. Of the commonly used reactions, the Suzuki-Miyaura (SM) coupling has been proven to be the most useful and widely applied [1]. Our efforts have been mainly devoted to the development of new Pd-based catalysts that can efficiently promote the SM reaction in mild and green conditions. The focus of interest is: i) use of safe solvents, ii) room temperature catalysis, iii) reusability of the catalytic system.

In recent work from our group, the Pd/CeO_2 system was found to show very good activity for the SM coupling in water/ethanol mixtures at room temperature [2]. We demonstrated that the "heterogeneous" Pd-containing precatalyst acts as "releaser" of "homeopathic" amounts of a catalytically active soluble form of Pd. Furthermore, we succeeded in recycling the Pd/CeO_2 precatalyst at least ten times without a marked decrease of catalytic activity.

The present work is an extension of the study to different Pd/Ln_xO_y catalyst precursors (Ln = La, Pr, Sm, Gd, Dy and Yb). Interestingly, all novel catalytic systems showed an activity much higher than that exhibited by Pd/CeO_2. The reusability of all precatalysts is also good, in particular for Pd/Sm_2O_3.

Current studies are focused on assessing some crucial features of the mechanism of formation of the "true" catalyst. In particular, the higher catalytic activity of Pd/Ln_2O_3 with respect to Pd/CeO_2 seems to be related to the easier release of Pd particles from the surface of the former precatalyst.

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INO/OM-OR-02 New tetracene based materials for organic electronics: organometallic approach to their synthesis.

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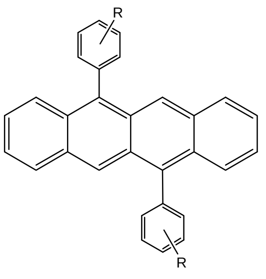
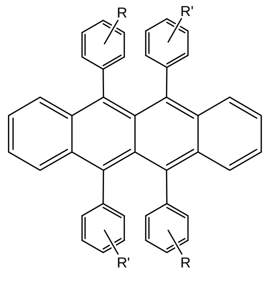
Acene-based organic semiconductors, thanks to their outstanding properties and their good processability, are key molecular materials for the development of organic electronics and derivatives of tetracene represent those where a good compromise between environmental stability and charge transport solid state properties is realised. Among tetracene-based systems, rubrene (5,6,11,12-tetraphenyl-tetracene) showed exceptional high charge carrier mobilities in Organic Field Effect Transistors (OFET) built on single crystals[1] and now represents the state of the art for molecular organic semiconductors.

It is noteworthy that, despite the peculiar and interesting properties of aryl-substituted-tetracenes, few synthetic routes are available (mostly tedious multi steps procedures) and relatively limited examples of molecules belonging to this series are known. This should urge on the organic chemist community to develop synthetic strategies to access to new organic semiconductors belonging to this class with improved transport properties, stability and processability. In principle, these properties (stability against photo-oxidation, solubility and charge carrier mobility) can be optimized by proper chemical modifications both on the tetracene core and on the aryl-substituents and transition metal-catalyzed processes are, from this point of view, particularly appealing both to improve the efficiency and to shorten the synthetic procedures.

Here we present our advances on the synthesis of new diaryl- and tetraaryl tetracenes where Pd-mediated cross-coupling reactions represent the key tools both to access to these systems and to prepare strategic precursors. In particular the synthesis of 1,1,3-triaryl-substituted propargyl alcohols, key intermediate for the synthesis of 5,6,11,12 tetra-aryl-substituted tetracenes (Rubrene-like systems) by copper-free Sonogashira protocol along with their evolution into rubrenes will be described.[2] A new protocol for the preparation of 5,11-diaryl-substituted tetracenes by Suzuki-based cross-coupling reaction from 5,11-di bromo- tetracene in liquid ionic will be also presented.[3] Some properties of the new tetracenes will be discussed.



5,11-diaryl-tetracenes



5,6,1,11,12-tetraaryl-tetracenes

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INO/OM-OR-03 Organometallic Fuel Cell development: the combined effect of molecular architecture with an high surface area carbon support

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The selective and simultaneous conversion of alcohols and sugars into energy and chemicals is a target of primary importance for the sustainable development. Two established types of fuel cells operating in alkaline media can convert the free energy of alcohols (R-CH_2-OH) into electrical energy and the corresponding carboxylate product: the direct alcohol fuel cell (DAFC), based on feasible metal electrocatalyst for alcohol oxidation [1] and the enzymatic biofuel cell (EBFC) that utilizes oxidation enzymes such as dehydrogenases in conjunction with an electron transfer mediator [2]. From a mechanistic viewpoint, the conversion of ethanol into energy and acetate resembles the process occurring in a biofuel cell where the electrocatalytic system consists of alcohol- and aldehyde-deydrogenases in combination with a hydrogen/electron transfer mediator. Recently, we introduced a third type of fuel cell operating in alkaline media where the anode catalyst is *a molecular metal complex.* We showed that in this device, named “organometallic fuel cell (OMFC)” a molecular rhodium complex is capable of evolving through fast chemical equilibria in the course of the catalytic cycle to form a specific catalyst for alcohol dehydrogenation, a specific catalyst for aldehyde dehydrogenation and a specific catalyst for the H/electron-transfer [3]. From a practical perspective, a molecular metal complex, soluble in different solvents and hence easily dispersible on very small surfaces, but capable of delivering high power densities upon oxidation of alcohols and sugars, paves the way to the further miniaturization of fuel cells for biological applications as well as biosensors. The combination of *well-defined molecular architecture* with a *matching support* (high surface area carbon black types) might allow for the selective oxidation of polyalcohols into valuable chemicals under waste-free conditions which is hardly achievable by traditional methods.

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INO/OM-OR-04 Microwave-Assisted Aminocarbonylation of Ynamides using catalytic $Fe_3(CO)_{12}$ at Low Pressure of Carbon Monoxide

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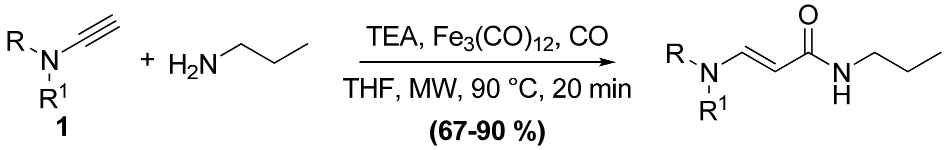
Carbonylation is a wideley applied atom economic reaction providing esters, ketons, carboxylic acids, amides and heterocyclic compounds.[1] Several procedures for the carbonylation of alkene and alkyne derivatives with different catalysts have been investigated but only few reports investigate the use of iron as the catalyst.[2] Iron carbonyl complexes have been increasingly used in organic synthesis in recent years and iron catalysis represents a promising area in the homogeneous catalysis.

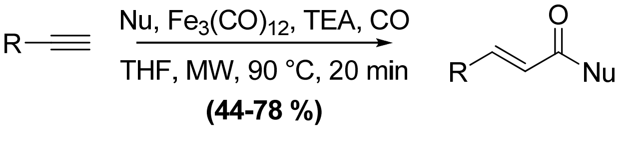
Beside our interest on new ecofriendly catalysts for microwave assisted carbonylation reactions using carbon monoxide as a bening source of C, a microwave-assisted procedure for the iron catalyzed carbonylation of ynamides and terminal alkynes was developped.[3]

Starting from ynamides **1** a new class of *E*-acrylamides has been regioselectively synthesized after irradiation with microwaves for only 20 minutes at low pressure of CO (1.3 bar) using $Fe_3(CO)$ and TEA as the catalyst precursors (Scheme 1).



Scheme 1

The same procedure can be easily applied to terminal alkynes giving regioselectively *E*-acryl- and cinnamides. Using alcohols or thiols as nucleophiles *E*-acrylesters and thioesters are obtained in good yields as well (Scheme 2).



Scheme 2

The building blocks obtained by this atomeconomic process are key intermediates in the synthesis of natural products and small bioactive molecules.

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ORG/OM-IL-01 Metal Nanoparticles as Efficient Catalysts in Green Chemistry

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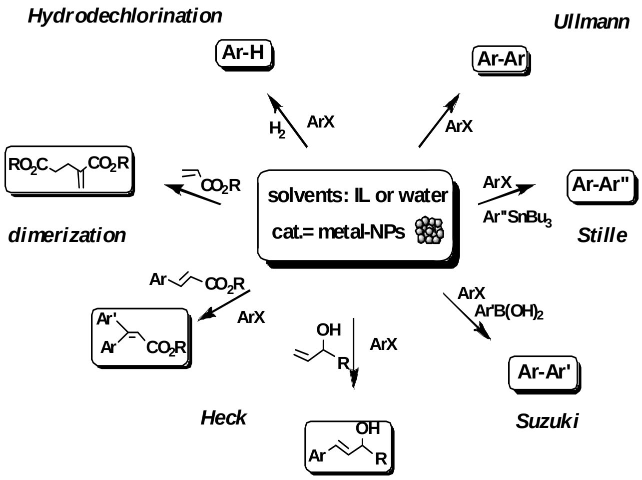
Transition-metal nanoparticles (NPs) are attracting a great deal of attention in almost any scientific and technological field, including catalysis, where nanoscale materials are becoming more prevalent in a wide range of applications such as fuel conversion, pollution abatement and fine chemical production.[1]
An increasing interest is also devoted nowadays to properly exploit the high activity and selectivity of nanocatalysts in order to develop greener and waste-minimized processes. From the Green Chemistry standpoint, new nanocatalysts must be designed to operate under environmentally friendly (for instance phosphine-free) conditions or in neoteric green solvents (e.g. ionic liquids, supercritical fluids, fluorous phases, water and so on).[2]



In this context, during the last decade, we exploited the use of nanostructured metal catalysts based on palladium, copper, and gold, to perform a wide range of C-C bond forming reactions, like for example Heck, Suzuki, Stille, acrylate dimerization, and Ullmann couplings, using tetraalkylammonium ionic liquids and water as green reaction media.[3]

This communication deals with our recent advances in controlling the catalyst performances by choosing appropriately the nature of the ionic liquid or the aqueous medium.

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ORG/OM-IL-02 The Amination of Hydrocarbons Catalysed by Ruthenium Porphyrin Complexes. A Mechanistic Investigation.

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The direct amination of hydrocarbons is a reaction of great synthetic interest due to the biological and pharmaceutical importance of aza-derivatives. We have focused our interest on this class of transformations for ten years using aryl azides as nitrogen sources and metallo porphyrins as catalysts [1]. More recently, we have investigated the catalytic activity of Ru(TPP)CO in C-H bonds aminations and we have isolated and characterised the active bis-imido intermediate Ru(TPP)(NAr)$_2$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) (**1**) [2].

To propose a general mechanism for the reaction we have investigated the reactivity of Ru(TPP)CO (**2**) towards several aryl azides, discovering that the nature of the active intermediate strongly depends on the electronic nature of the employed azide. The replacement of 3,5-(CF$_3$)$_2$C$_6$H$_3$N$_3$ with 4-CF$_3$C$_6$H$_4$N$_3$ in the reaction with Ru(TPP)CO allowed the isolation of the mono-imido complex Ru(TPP)(NAr)CO (Ar = 4-(CF$_3$)$_2$C$_6$H$_4$) (**3**) that showed a good catalytic activity in hydrocarbon aminations. On the other hand, the reaction of Ru(TPP)CO with an aryl azide bearing an electron donating group, 4-^{t}BuC$_6$H$_4$N$_3$, gave a very unstable imido complex (**4**). Complex **4** has been detected by NMR and it rapidly decomposed to the mono-amino compound Ru(TPP)(NH$_2$Ar)CO (Ar = 4-^{t}BuC$_6$H$_4$) (**5**) that was isolated and characterised.

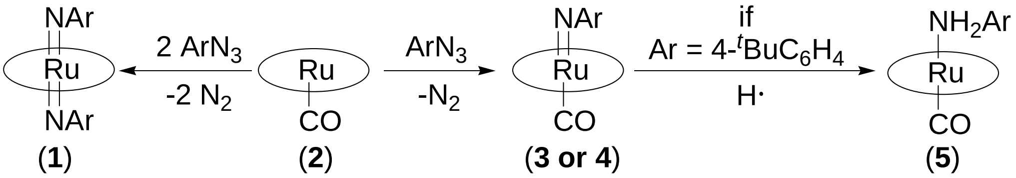

Figure 1

A kinetic study has been also performed to better rationalise the dependence of the reaction mechanism on the nature of the organic azide.

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ORG/OM-OR-01 Cationic Olefin Complexes of Platinum(II): from the Well Established to New Perspectives

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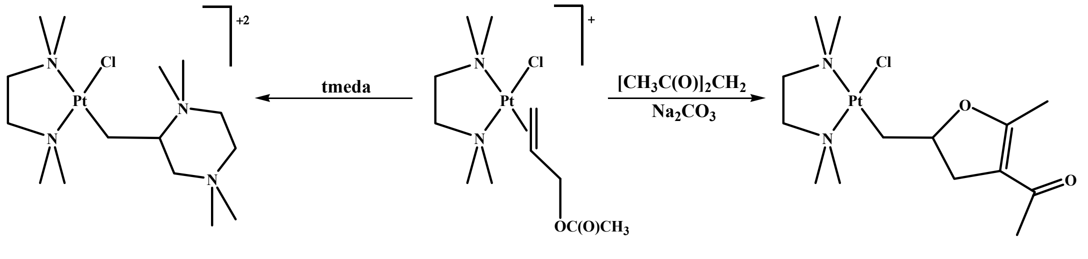
After our first report concerning the complex $[PtCl(\eta^2\text{-}C_2H_4)(N\text{-}N)]^+$, **1**, (N-N = *N,N,N′,N′*-tetramethylethanediamine, tmeda) [1] many properties of this type of species have been clarified.

The obtainment of **1** (the prototype of stable cationic platinum complexes which can contain olefins different from ethene) was a clear experimental proof of the σ-donating properties of olefins, which could give stable complexes also in the absence of relevant π-back-donation from the metal to the unsaturated ligand.

The coordinated olefin is endowed with a good degree of electrophilicity [2] and, in the case of olefins higher than ethene, it can also exhibit Brönsted acidity [3]. Deprotonation can eventually prevail over nucleophilic addition [4].

The dinitrogen ancillary ligand plays an important role in tuning the properties of the complexes; in particular, when tmeda is replaced by an aromatic diimine, the metal becomes more electrophilic and it can compete with the olefin in the reaction with soft nucleophiles [5].

In cationic complexes with allyl acetate, $[PtCl_2(\eta^2\text{-}CH_2{=}CHCH_2OC(O)CH_3)(N\text{-}N)]^+$, two reactive sites are present in the coordinated olefin: the allylic carbon and the C=C double bond. Nucleophiles first replace the acetato group and then add to the olefinic bond. In the case of bidentate nucleophiles a heterocycle is built up in the near proximity of the coordination sphere (see Scheme). When the two donor atoms are different, because of the two consecutive reaction steps, only one of the possible isomers is formed.



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ORG/OM-OR-02 Sustainable Oxidations with Tailored Molecular Metal Oxides: Bridging the Gap between Homogeneous and Heterogeneous Catalysis

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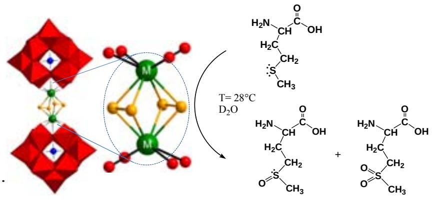
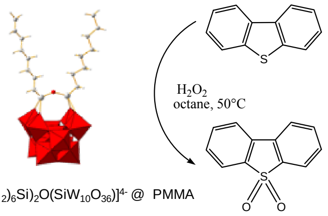
Polyoxometalates (POMs) have been proposed as the homogeneous models of solid metal oxides. Their success of as oxidation catalysts is based on their multi-metallic composition, which is pivotal to access diverse mechanistic pathways and an enhanced stability. The presence of d^0 metals, in particular, can be exploited to activate the non-waste producing oxidant H_2O_2. We present herein two promising strategies to design innovative and sustainable oxidative processes with H_2O_2, involving the use of transition metal substituted POMs (TMSPs) and hybrid organic-inorganic POMs.

(i) The molecular structure of TMSPs, featuring well defined catalytic sites, may be very convenient to study the mechanism and to tune their reactivity. Stable dimeric POM structures containing 4th group transition metals as Zr^{IV} or Hf^{IV}, in particular, form peroxometal-butterflies as active species. They have been used in water to oxidize *L*-methionine (70-99% yields in 20-48 h, at r.t.) and benzyl alcohols (50 min, under MW assisted activation, T_{bulk}=90°C, TOF= 75 h^{-1}) [1].



(i).



(ii). $[(CH_2{=}CH(CH_2)_6Si)_2O(SiW_{10}O_{36})]^{4-}$ @ PMMA

(ii) Covalent grafting of organic moieties on POMs may implement affinity towards different media, as well as immobilization strategies [2]. POMs functionalized with unsaturated alkyl chains have been used as monomers to prepare methacrylate-based copolymers, by means of radical polymerization. The heterogeneous catalytic material has been used to model a fuel desulfurization process: in octane, dibenzothiophene has been quantitatively converted to the corresponding sulfone in 4h (TOF= 18 h^{-1}).

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ORG/OM-OR-03 Evaluation of counterion and solvent effect in the single insertion of olefin into the Zr-C bond by low-temperature NMR kinetic studies

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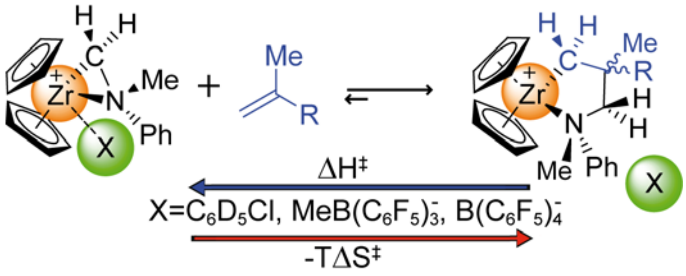

The insertion of olefin into the metal-carbon bond is the elemental step of the Ziegler-Natta catalysis that, in the homogeneous phase, occurs through the initial association of the olefin with the metal cation of the catalytic ion pair. Group IV metallocenium ion pairs polymerize olefins with high rates, but the elevate reactivity of such systems dramatically complicates fundamental kinetic investigations. During our studies on the self-aggregation of zirconocenium ion pairs [1,2], we synthesized some zirconazidirines having ($[Cp_2Zr(\square^2\text{-}CH_2\text{-}NR_1R_2)][X]$ as general formula that show some remarkable requisites to be used as good models for investigating the single insertion of olefin into the Zr-C bond. In particular, they are able to react stoichiometrically with olefins leading to a five-membered azametallacycle, as represented in figure.

With the aim of obtaining thermodynamic activation parameters of the single insertion and determining as they depend on nature of counterion and solvent, low-temperature kinetic NMR studies of the reaction of 2-methyl-1-heptene with $[Cp_2Zr(\square^2\text{-}CH_2\text{-}NMePh)][X]$ [**1a**:X^- $=MeB(C_6F_5)_3^-$; **1b**:$B(C_6F_5)_4^-$] ion pairs were performed. Results indicate that, in toluene, $\square H^{\ddagger}$ is higher for $MeB(C_6F_5)_3^-$ than for $B(C_6F_5)_4^-$ ($\square\square H^{\ddagger}=-4.5$ kcal mol^{-1}) but the former better compensates the loss of entropy caused by olefin association ($\square\square S^{\ddagger}=-13$ cal mol^{-1} K^{-1}). The two ion pairs **1a-b** behave exactly the same in a toluene/chlorobenzene mixture due to the coordination of a chlorobenzene molecule at the zirconium center that pushes the counterion in the second coordination sphere. $\square H^{\ddagger}$ (ca 11 kcal mol^{-1}) is higher than in toluene ($\square H^{\ddagger}=8.5$ kcal mol^{-1} and $\square H^{\ddagger}=4.0$ kcal mol^{-1} for **1a** and **1b**, respectively) while $\square S^{\ddagger}$ (ca -26 cal mol^{-1} K^{-1}) is similar to that of **1a** in toluene ($\square S^{\ddagger}=-32$ cal mol^{-1} K^{-1}).

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ORG/OM-OR-04 Synthesis and application of Tetraferrocenylporphyrins as sensitive materials in photoelectrochemical devices

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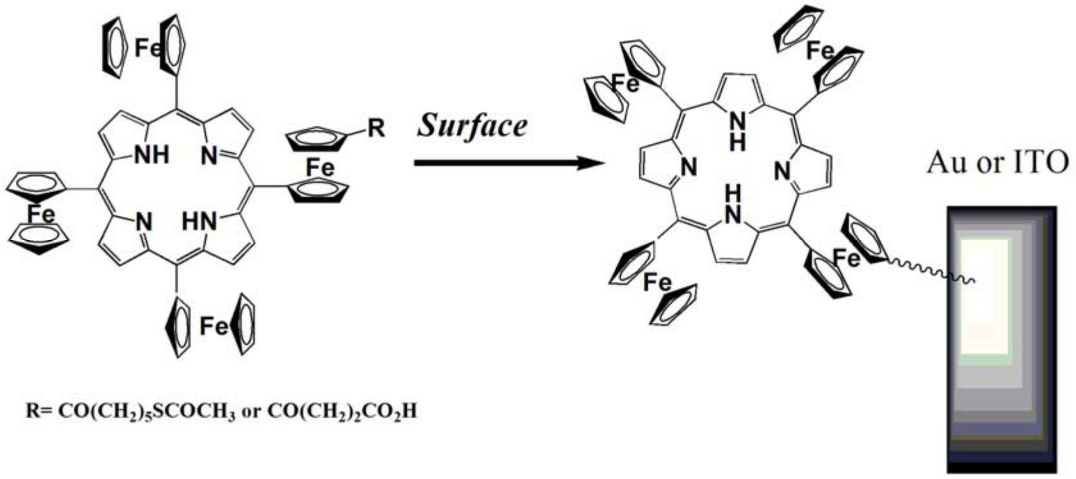
5,10,15,20-tetraferrocenylporphyrins have been object of our interest in different application such as electron transfer reactions [1], mixed-valence states [2], multiredox processes and long-range electronic internal communication [3]. These properties make them suitable for the construction of photochemical devices.

New tetraferrocenylporphyrins containing one functionalized ferrocenyl group were synthetized with the aim to link these molecules on surfaces. A chain with a terminal thioacetate or carboxylic acid was used to obtain functionalized Au or ITO surfaces.



R= $CO(CH_2)_5SCOCH_3$ or $CO(CH_2)_2CO_2H$

The obtained monolayers were characterized by Uv-vis and electrochemical techniques and used in photoelectrochemical cells. Promising results in terms of photocurrent vs applied potential was obtained and will be discussed in connection with the surface-potential-experimental conditions set.

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INO-PO-01 Structural electronic study via XPS and TEM of sub-nanometric gold particles protected by calixarenes

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Metal nanoparticles (NPs) arise high scientific interest because they display unique properties, relevant in many established or emerging fields as optoelectronics, catalysis and sensing. An attractive property of NPs is their ability to anchor onto the core suitable receptors in a radial 3-D arrangement for the recognition of species [1]. Gold nanoparticles (AuNPs) are the most stable metal NPs, and their production as ligand-covered clusters constitutes a class of emerging hybrid organic-inorganic materials. In particular, thiol-stabilized AuNPs have become a model system in nanomaterials research due to their stability, easy preparation and chemical versatility [2].

A series of differently sized AuNPs stabilized by monodentate, bidentate, tridentate and tetradentate thiolate calix[4,6]arene ligands, prepared by the Brust-Schiffrin two-phase synthesis, were characterized by XPS, in combination with TEM. The experimental data show that the multidentate structure of calixarenes introduces a control element in the preparation, which is crucial to obtain very small (< 1 nm) AuNPs [3]. The core size distribution of the clusters was determined by analyzing TEM images. XPS measurements allow to separate the Au atoms in two subsets, on the basis of their clearly distinct Au 4f binding energy: Central Atoms, at 82.8-83.5 eV, and Surface Atoms bound to S, falling at 1.3 eV from central Au. These values suggest that S ligands attract positive charge on surface leaving a more negative inner atom. The S 2p spectra present a main component due to thiolate-Au bond, compatible with the structural "Staple Motif" reported in the literature [4]. Since very small NPs have a larger percentage of surface atoms, the experimental S/Au and Au-S/$Au_{central}$ ratios are an indirect evaluation of the cluster nuclearity, likely to be assigned to Au_{11} or Au_{13}, both compatible with the observed diameters.

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INO-PO-02 Synthesis, X-ray Crystal Structures and Magnetic Studies of Oligonuclear Manganese(III) and Iron(III) Compounds with 'Strained' Schiff Base Ligands

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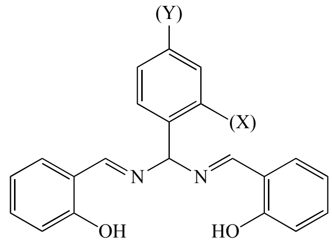
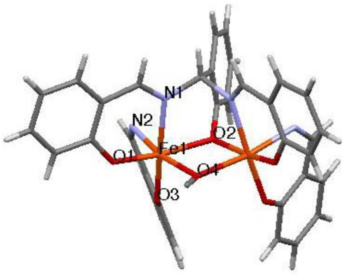
The synthesis and the study of oligonuclear transition metal compounds has been a very active field in the last years, mainly addressed to the comprehension of the spin communication pathways for their potential application as molecular magnets [1].



H_3salmp (X = OH, Y = H)
H_2sal(*o*-X)ben (X = OMe, Cl, NO_2, Y = H)
H_2sal(*p*-Y)ben (X = H, Y = ^{t}Bu, Me, H, F, Cl, CF_3, NO_2)

Few years ago our research group started a systematic approach to this regard using 'strained' tetra- and pentadentate Schiff base ligands (namely the H_2salben and the H_3salmp types, respectively) derived from the condensation of two salicylaldehydes with arylmethandiamines [2]. They possess only one carbon atom between the two donor iminic nitrogen atoms, favouring the formation of di- or oligonuclear complexes.

The reaction between this kind of ligands with manganese(III) and iron(III) yields compounds whose nuclearity ranges from dinuclear to tetranuclear, depending on the reaction solvent, the substituent position on the ligand and the deprotonating base used.



Crystal structures of some derivatives, and the magnetic studies of the most representative cases will be also reported.

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INO-PO-03 Xenon-Nitrogen Chemistry: Gas-phase Generation by ITMS and Theoretical Investigation of the Xenon-Difluoronitrenium Ion $F_2N\text{-}Xe^+$

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The xenon-difluoronitrenium cation $F_2N\text{-}Xe^+$, a novel xenon-nitrogen species, is obtained in the gas phase by the nucleophilic displacement of HF from protonated NF_3 by Xe. MP2 and CCSD(T) theoretical calculations reveal that this process is exothermic and exoergic by ca. 3 kcal mol^{-1}. The conceivable alternative formation of the inserted isomer $FN\text{-}XeF^+$ is instead endothermic by as much as 40-60 kcal mol^{-1}, and is not attainable under the employed ion trap mass spectrometric (ITMS) conditions. $F_2N\text{-}Xe^+$ is theoretically characterized as a weak electrostatic complex between NF_2^+ and Xe, with a Xe-N bond distance of 2.4-2.5 Å, and a dissociation enthalpy and free energy into its constituting fragments of 15 and 8 kcal mol^{-1}, respectively. $F_2N\text{-}Xe^+$ is therefore more fragile than the xenon-nitrenium ions $(FO_2S)_2NXe^+$, $F_5SN(H)Xe^+$, and $F_5TeN(H)Xe^+$ observed in the condensed phase as AsF_6^- or $Sb_3F_{16}^-$ salts [1-4]. It is however still stable enough to be observed in the gas phase. Other otherwise elusive xenon-nitrogen species could be obtained under these experimental conditions.

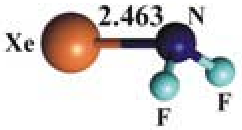

Figure 1. $F_2N\text{-}Xe^+$. The bond distances (Å) are optimized at the MP2/def2-TZVPP level of theory.

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INO-PO-04 Synthesis and Properties of Achiral Asymmetric Dinuclear Tris(1-pyrazolyl)methane Complexes of Ru(II).

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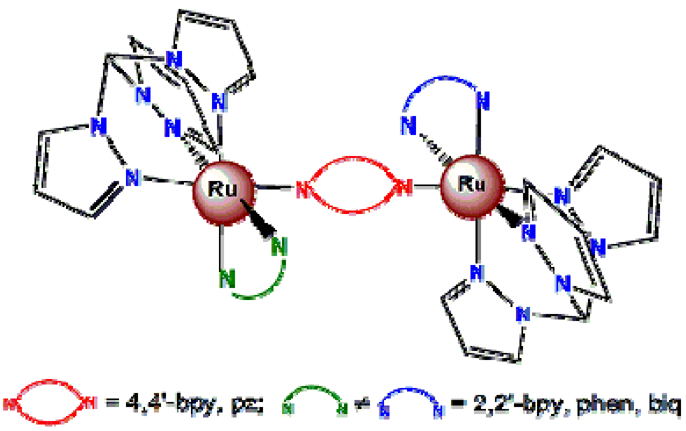
Exploiting the “complexes-as-metals/complexes-as-ligands” synthetic strategy [1] a family of six novel polypyridyl dinuclear species containing two different Ru(tpm)(CL) units [tpm = tris(1-pyrazolyl)methane, CL = 2,2’-bipyridine, 1,10-phenanthroline, 2,2’-biquinoline] bridged either by 4,4’-bipyridine or pyrazine (see the chart) have been prepared as hexafluorophosphate salts.



These compounds re-present the asymmetric analogues of six dinuclear complexes whose synthesis and properties have been recently published [2]. No-tably, owing to the presen-ce of a tripodal ligand, the metal centres are not chiral, thus the samples are not diastereomeric mixtures, a feature that prevents the structural characterization of oligonuclear trischelate complexes [3].

All novel complexes have been thoroughly characterized by elemental analyses and IR spectroscopy, and their ^{1}H NMR spectra completely assigned on the basis of COSY and NOESY experiments.

The photophysical, electrochemical, and spectroelectrochemical properties of the new species will be reported and discussed in terms of their similarities and differences with respect to those observed for their symmetric analogues.

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INO-PO-05 {[Cu_2(*bis*-tren-*ter*-2,5-dimethylfurane)(Cl)]$^{3+}$/[1.1.1]Cryptand}: A Prototype of Composite Kinetic Molecular Device for Slow Anion Releasing

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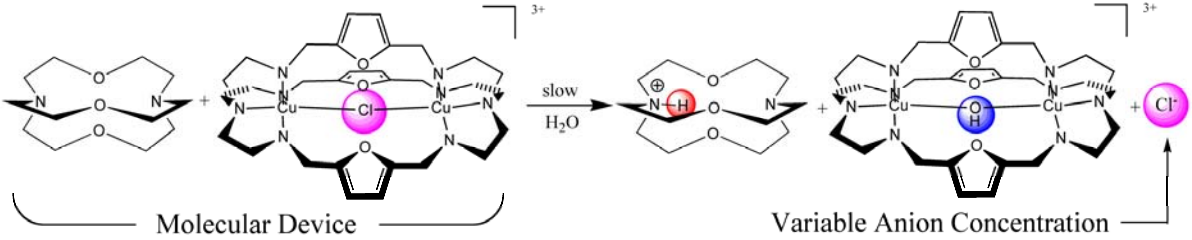
Kinetic molecular devices (KMDs) perform a specific work at a molecular level by using the kinetics of the process in which they are involved. Particularly, variable-parameter kinetic molecular devices (VPa KMDs) are able to change in a controlled way an environmental parameter (pH, *T, I,* [Nu], etc.) inside a reaction vessel making it possible to follow automatically parameter-sensitive processes without using external physical devices.[1] Variable-pH and variable-temperature KMDs have been used to carry out, respectively, spectrophotometric and NMR variable-pH kinetic experiments or automatic titrations and variable-temperature kinetic experiments. In some cases *cooperative* composite KMDs have been used, formed by two chemical systems working as a molecular apparatus, able both to change the parameter and to monitor it.[2]

In this contribution a first example of *integrated* composite KMD is proposed where two chemical devices operate together in the same environment, interacting with each other, to perform a work different from those peculiar to the single ones. It is formed by [1.1.1]cryptand,[3] able to change slowly and irreversibly the pH in a linear way,[1] and [Cu_2(*bis*-tren-*ter*-2,5-dimethylfuran)]$^{4+}$, able to capture rapidly and reversibly anions (Cl^-, Br^-, I^-, N_3^-).[4] The two devices, together, act as a variable-anion concentration KMD by releasing slowly and almost linearly with time anions, in this way making it possible to follow automatically anion-sensitive processes without using physical devices.



A mathematical model has been derived to describe the behavior of this complex system and a computer simulation for various anions in various conditions has been carried out. A spectrophotometric method to follow the concentrations of the involved species and the pH has been devised.

An experiment has been carried out in a 1 mm quartz cuvette containing, in water at 25°C, [1.1.1]cryptand 0.1 M, [Cu_2(*bis*-tren-*ter*-2,5-dimethylfuran)]$^{4+}$ 0.003 M and Cl^- 0.003 M. The change in absorbance, processed by the mathematical model, gave, without using external pH and anion sensors, the increasing values of both pH and chloride concentration.

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INO-PO-06 (2-Pyrene-1-yl-vinyl)pyridine: a highly transparent chromophore with an unexpected large second-order nonlinear optical response

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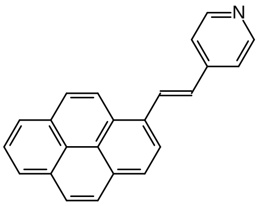
In the field of electrooptic materials, the rational design and synthesis of chromophores endowed with high transparency together with large second order nonlinear optical (NLO) response is a field of intense research activity. Many organic and metallorganic second order NLO chromophores have been designed according to the ''push-pull'' strategy, where electron-donating (D) and electron-withdrawing (A) end groups interact through a delocalized π-electron bridge to generate an intramolecular charge transfer transition [1]. On the other hand, far less attention has been devoted to low dipole moment chromophores, though in some instance they have been shown to possess large hyperpolarizability β [2].

Here we report on the second order NLO properties of (2-pyrene-1-yl-vinyl)pyridine, **1**, a chromophore based on the pyrene moiety which is well studied for its outstanding fluorescence properties (long lifetime and high quantum yield) while its derivatives have never been investigated for their NLO response. Preliminary measurements of the second order NLO properties of **1** in solution by the EFISH technique revealed an unexpectedly high and strongly concentration dependent μβ value, comparable to that of benchmark NLO chromophores. At high concentrations the decrease of the second order NLO response seems to point to the formation of centrosymmetric aggregates, a feature that is supported also by the emissive behaviour of **1**. Interestingly **1** is quite transparent, a relevant property for potential technological applications. These experimental results have been supported by theoretical investigation performed at DFT and Time Dependent DFT level, which has allowed an analysis of the electronic origin of the NLO response.



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INO-PO-07 Dynamic behaviour of Pd and Pt tiourea complexes

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Pd^{II} and Pt^{II} thiourea complexes are a crucial topic in inorganic chemistry for the peculiar kinetic and thermodynamic features and for biological properties related to their anti-cancer activity [1-2]. As a matter of this fact, the strong binding ability of these S-donor nucleophiles is currently exploited in chemotherapy to reverse unwanted side effects of Pt-based drugs [3-4]. A typical feature of the S coordinated thiourea is the M-S=C angle (ranging from 106 to 118°) which, in the case of rigid square planar complexes, pushes the thiourea ligand over the coordination plane along a roughly perpendicular plane [5,6]. NMR multinuclear (1H, 13C, 15N and 195Pt) analysis at variable temperature demonstrate that complexes $[M(\overset{\frown}{NN})(n\text{-}TU)]Cl_2$ (M= Pd^{II} or Pt^{II} ; $\overset{\frown}{NN}$= 2,2'-bipyridil or phenanthroline; n-TU = alkyl substituted thioureas) do show many different conformations in a temperature tunable exchange according to C=N and M-S hindered rotation or S inversion. The $[M(\overset{\frown}{NN})(n\text{-}butyl\text{-}TU)]Cl_2$ ^{13}C and inverse detected ^{15}N at 225°K show the presence of four conformers. Pulse gradient HMBC-^{15}N detections [7] took great advantage by a large unespected β-C-H long-range coupling (^{3}J) with nitrogen. An important NMR feature of these complexes (also in view of their biological activity) is the proton donor capability leading to a reversible decrease of the positive charge during the cell membrane-crossing.

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INO-PO-08 Nanostructured functional copolymers bioconjugate integrin inhibitors

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Polymeric materials with nanosized structures and self assembly properties have been previously achieved by emulsion polymerization and osmosis based methods[1,2].

Synthesis and properties of bioconjugates based on functionalized polymeric nanoparticles (PNs) and monoclonal anti-Integrin αV CD51 (aI) antibody were now investigated. Polymeric and co-polymeric colloidal nanoparticles with different functionalities, i.e. acid, amine or thiol, namely poly(methylmethacrylate-co-acrylic acid) [P(MMA-co-AA)], poly(methylmethacrylate-co-dimethylpropargylamine) [P(MMA-co-DMPA)], poly(methylmethacrylate-co-allil mercaptane) [P(MMA-co-AM)], were obtained by tailoring emulsion synthesis and fully characterized by means of spectroscopic techniques and scanning electron microscopy (SEM). Bioconjugates (PN/aI) based on P(MMA) or P(MMA-co-AA) were obtained by loading the polymeric nanoparticles with the antibody anti-Integrin with a simple and straightforward immobilization strategy. Qualitative and quantitative loading analyses of bioconjugates were carried out by means of polyacrylamide gel electrophoresis 1D-PAGE, MALDI-TOF and LC/ESI-MS/MS investigations. The biological efficacy of bioconjugates was confirmed by the reduced migration potential of PN/aI-treated human kidney cells (HEK293). The easy immobilization procedure and high immobilization capacity of polymeric nanoparticles together with tuneable chemical functionalities and dimension of the polymeric nanoparticles open applicative perspectives for targeted delivery.

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INO-PO-09 Conjugated Pt-Containing Polymetallaynes for gamma-Radiation Dosimetry

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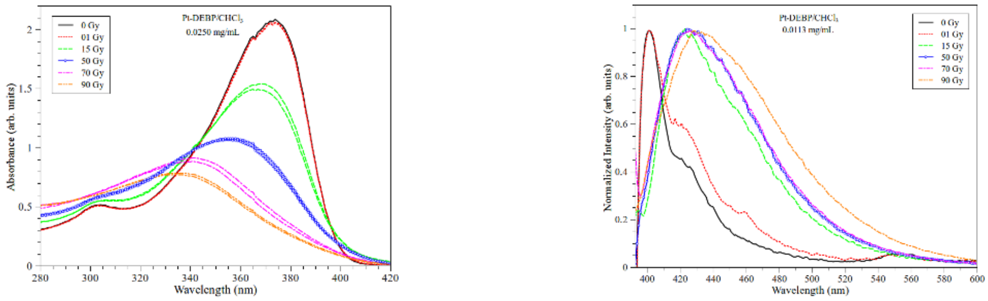
Polymetallaynes show peculiar properties that allow their use in electronic and electro-optical devices sensors and biosensors, electroluminescence and photovoltaic behavior [1]. On the basis of our previous research [2], we report a new application, *i.e.* the gamma rays detection achieved by a Pt containing polymetallayne, Pt-DEBP. This polymer can be used as γ rays dosimeter for doses higher than 15 Gy using the absorption spectra changes. Shifts in the position of the main peak of the absorption spectrum of the solutions had an approximately linear relationship. Changes in the fluorescence spectrum suggest that the system can also be used for doses below 1 Gy (Figure 1, a-b).



a- Optical absorption spectra of Pt-DEBP *b- Emission spectra of Pt-DEBP*

The spectra have been recorded before and after irradiation with γ rays at different radiation doses.

The response of Pt-DEBP to increasing gamma ray exposure has been interpreted as due to the fragmentation of the polymer backbone, likewise the case of already investigated polymers. Theoretical studies have supported our preliminary assessments. In fact, we have fully characterized by TDDFT calculation the absorption spectrum by comparison with a very similar model system.

Acknowledgements. The authors gratefully acknowledge the financial support of this research by MAE-MIUR Progetti di Ricerca Scientifica e Tecnologica Bilaterale 2008-2010, CNPq (Brazil), FAPESP (Brazil) and CNEN (Brazil).

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INO-PO-10 Studies on nickel selenite and related complexes: structural features, magnetic properties and reactivity

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There is a growing interest in the structural chemistry of selenites and tellurites, due to the following properties: (1) the ability to produce solid state structures containing channels and cavities suitable to housing the chalcogen electron lone pair, (2) the ability of the chalcogenite anion to act as a bridge between two transition metal cations, permitting magnetic exchange between paramagnetic centres, (3) the possibility of the chalcogen electron lone pair to give rise to supramolecular interactions.[1]

By reacting $Ni(NO_3)_2$ with Na_2SeO_3 in presence of tetramethylethylenediamine (TMEDA) the heteroleptic dinuclear complex $[Ni(\mu\text{-}SeO_3)(TMEDA)]_2\cdot 8H_2O$ is obtained. It consists of a dinuclear species in which the two nickel atoms are held together by two bridging selenito anions and 6 water molecules are involved in hydrogen bonds directly with the oxygen atoms of the selenite anions. The two nickel cations exhibit antiferromagnetic coupling with $J = -25.7 \pm 0.1\ cm^{-1}$, in good agreement with the DFT calculated value of $-27\ cm^{-1}$ for the $[Ni(\mu\text{-}SeO_3)(TMEDA)]_2\cdot 6H_2O$ species. The coupling between the two metals occurs primarily via the bridging oxygen atom O(1) and also to a minor extent through the O-Se-O bridge, as attested by the spin density distribution.

Regarding the simple selenite salt $NiSeO_3$, it has been reacted with CO with the aim to produce NiSe: the obtained materials have been studied by IR, XRD and XPS.

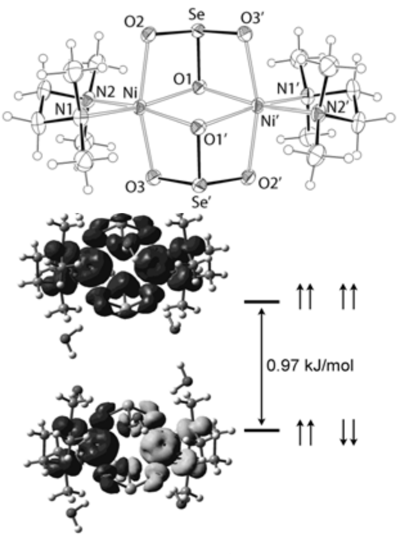

Figure 1. Crystal structure and energy levels of the antiferromagnetic quintet with hydrogen bonded water molecules.

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INO-PO-11 Unexpected Isomerism in "[Pd(2,9-dimethylphenanthroline)X_2" Complexes: Not Always the Same Compound

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Complexes bearing the 2,9-dimethylphenanthroline (neocuproine, Neoc) ligand have attracted a special attention because the steric hindrance caused by the two methyl groups stabilizes unusual coordination geometries and the formation of otherwise unstable adducts. Such feature is also essential to allow high catalytic activity in some reactions. Among these, palladium-catalyzed oxidation reactions are surely worth mentioning. Palladium neocuproine halide complexes have been known for a long time and are often used as the starting material for the synthesis of more complex compounds. Different synthetic approaches have been reported for their preparation, but the products are invariably formulated as $Pd(Neoc)X_2$ (X = Cl, Br, I). While investigating the reactivity of these complexes, we realized that even apparently minor variations in the synthetic procedure led to products that displayed completely different solubility behaviours despite having the same elemental analysis, always in excellent agreement with that calculated for the expected product. We thus engaged in a more in depth investigation of the identity of these apparently trivial compounds and found that two bonding isomers exist for each of the compounds in the series, one of which had escaped identification for more than 40 years, despite having previously been obtained by many researchers.

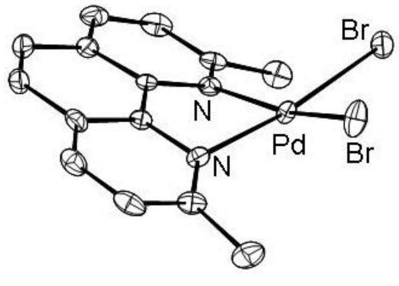

Figure 1. Neutral isomer: $Pd(Neoc)Br_2$

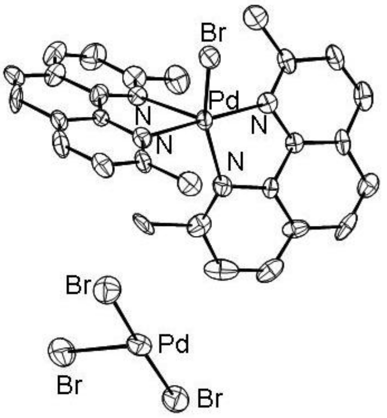

Figure 2. Ionic isomer: $[Pd(Neoc)_2Br]_2[Pd_2Br_6]$ (half of the crystallographic cell shown)

INO-PO-12 Synthesis and advanced characterizations of silver nanoparticles stabilized by organic thiols

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The functionalization of metallic nanoparticles (MNPs) surface with organic molecules allows for tuning the overall properties of particles in order to fit target applications. In this framework, the development of new strategies for the chemical stabilization of MNPs by means of specific ligands has been object of recent research. The chemical stabilization of MNPs by suitable organic ligands, i.e. the so called molecule-capping method, presents several advantages over other preparative methods such as low preparation costs and better NPs size, monodispersity and shape control. Among others, Au and Ag NPs can be functionalized with alkanethiol monolayers that afford high stability to the colloids against aggregation [1,2]. The synthesis and characterization of AgNPs of different sizes stabilized by allyl mercaptane (AM) is presented. The size-control of the AgNPs was achieved by direct control of synthesis parameters and the hybrids were characterized, among others, by means of synchrotron radiation-induced X-ray techniques as X-ray photoelectron spectroscopy (SR-XPS) and Extended Absorption Fine Structure spectroscopy EXAFS. XPS measurements were performed at the C1s, S2p and Ag3d core levels; EXAFS measurements were carried out at the Ag k-edge (25514 eV) and S k-edge (2472 eV). High resolution XPS measurements allowed to assess the anchoring of the thiols onto silver nanoparticles through a stable Ag-S bond. EXAFS measurements at the S k-edge provided further information about the thiols interaction with AgNPs, leading to hypothesize a core-shell system occurrence, with Ag_2S-like and Ag-S-R -like sulphur species, further suggested by SR-XPS S2p data. The EXAFS data collected at the Ag K-edge also provided information about the NPs dimensions and sizes dispersion.

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INO-PO-13 Push-pull Zn^{II}-porphyrin, *meso*-substituted with a benzodithiophene spacer, as promising sensitizer in Dye-sensitized solar cell.

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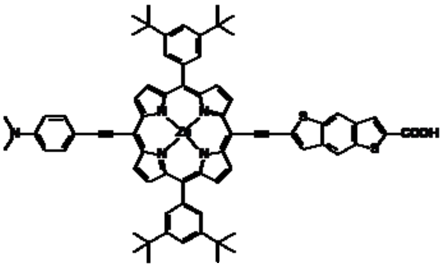
Dye-sensitized solar cells (DSSCs) represent today an interesting class of photovoltaic devices because of their excellent light-to-electricity conversion efficiencies. Many dyes have been investigated and among them the ruthenium sensitizers have shown the best results reaching more than 11% efficiency [1]. It was recently reported the achievement of an 11% efficiency with a push-pull *meso*-substituted Zn^{II}-porphyrin as dye [2].



Here we present the synthesis of a push-pull Zn^{II}-porphyrin with a N,N-dimethylaniline donor group and a carboxy acid acceptor group with a new benzo[1,2-b;4,5-b']dithiophene spacer.

The orthofused aromatic/thiophene system shows a rigid π-conjugated-condensed framework, free from configurational disorder, which leads to unique electronic properties such as conductivity, high field effect mobility and tunable stacking in the solid state relevant for applications such as in LED, FET and organic solar cells [3]. It may play a relevant electronic role in favoring electron transfer along the push-pull system.

Theoretical TD-DFT calculations, electrochemical and photoelectrochemical studies, and a compared investigation of the light-to-electricity conversion efficiency in a dye-sensitized solar cell will be presented.

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INO-PO-14 NEW TERNARY PHASES IN THE La–Ge–Mg SYSTEM

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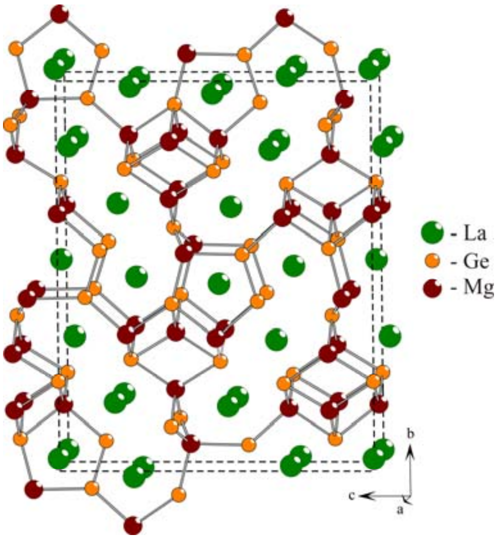
The R−X−Mg systems (R=rare earth metal; X=late transition metal or early post-transition metal) have been intensively studied in the last ten years with respect both to the fundamental and applicative point of view. Their scientific interest is mainly related to the fact that these systems show complex phase diagrams in which many ternary compounds exist, often characterized by peculiar structures, unusual stoichiometries and novel bonding features.

During the investigation of the La−Ge−Mg phase equilibria several ternary phases were detected and analyzed by our research group. The crystal structures of two of them, determined by single crystal X-ray diffraction analysis, are presented in this work: $La_4Ge_6Mg_5$ ($Gd_4Ge_6Zn_5$ str. type, *Cmc*2$_1$, *oS*60, *a*=4.5030(7), *b*=20.085(3), *c*=16.207(3) Å, Z=4) and $La_4Ge_6Mg_7$ (own structure type, *C*2/*m*, *mS*34, *a*=16.878(3), *b*=4.4702(9), *c*=12.660(3) Å, β=122.25(3)°, Z=4). Electronic structure calculations were performed applying the COHP formalism [1] within the LMTO method, in order to obtain information on chemical bonding.

Both phases are characterized by Ge−Mg distances close to the covalent radii sum (2.62÷2.84 Å); the bond strenghts of these contacts, expressed as – *i*COHP values, range from 1.22 to 1.96 eV per bond per cell and are the strongest in each structure. This makes it convenient to depict these compounds as formed by a 3D $[Ge{-}Mg]^{\delta-}$ polyanionic network balanced by electropositive La atoms. Such a network is outlined in the figure for $La_4Ge_6Mg_5$.



The negatively charged framework of typical polar intermetallics is formed by late transition metals and/or early post-transition metal elements close to the Zintl border. The peculiarities of Mg as an admix in the polyanionic network enriches the chemistry of polar intermetallics and allow one to rationalize the exploration of novel phases with desired properties.

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INO-PO-15 HYDROGENATION PROPERTIES OF MG–RICH La-Pd-Mg ALLOYS

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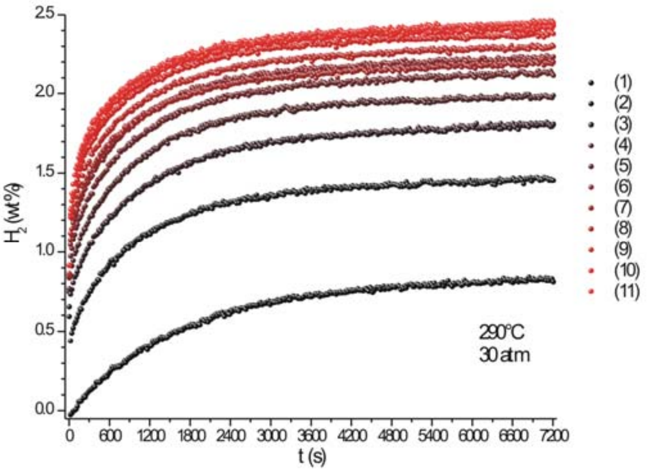
Numerous metals and alloys can absorb hydrogen by forming metal hydrides, some of which are currently being studied as H_2 storage systems in view of an increased use of this energy vector. Mg-based light hydrides are among the most investigated candidates for competitive hydrogen storage with sufficiently high reversible hydrogen capacity for mobile applications. Efforts have been particularly devoted to overcome the main disadvantages of pure Mg, such as the high desorption temperature and the slow kinetics [1]. To this purpose alloying magnesium with transition metals was considered and many binary or ternary systems based on magnesium were studied.

In this work the La-Pd-Mg system was targeted. Some La-Mg phases were already investigated with respect to hydrogenation [2]; on the other hand Pd itself has a great affinity for hydrogen and, similarly to other late transition elements, shows a significant reactivity with Mg and rare earth metals. The La_2Mg_{17} phase was therefore taken as starting composition, and ternary alloys were synthesized where Mg is partially substituted by Pd. Single-phase samples were obtained retaining an hexagonal crystal structure similar to the binary phase, as evidenced by X-ray diffraction analysis. Their hydrogen absorption/desorption behaviour was studied by a Sievert apparatus under different experimental conditions – as an example, the figure shows the increase of hydrogen capacity of a 4 at% alloy during the first 11 cycles – and it will be presented and discussed with respect to hydrogen capacity, desorption conditions, cyclability and structural changes induced in the material.



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INO-PO-16 Computational analysis of I-I bonds in the simplest polyiodides

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In the last decades, halogen bonding has acquired particular relevance for the building up of supramolecular patterns.[1] Heavier halides, especially iodines, are particularly sensitive to residual interactions, which allow formation of compounds of large nuclearities. In fact, anionic I_n^m species with n up 29 and m=-1,-2,-3 have been reported [2], the simplest one being obviously $I_3^{-.}$ Calculations of the electron density are available, which highlight the points of its accumulation/depletion hence the capabilities of subsequent aggregations [3]. From the MO point of view, it is important to understand the electronic parameters which affect the stereochemistry of the higher nuclearity assemblies and, in particular, the variable strengths of the I-I interactions. The variability of the effects are already observed in the simplest linear systems I_3^- and I_4^{2-}, of which there are numerous crystal structures available. The I-I distances significantly vary depending on the nature of the counterion(s) and the overall packing arrangement. Thus I_3^- has not always the expected $D_{\infty h}$ symmetry but the two distances can become as different as 0.2 Å. Also for I_4^{2-}, which in principle consists of a central I_2 molecule residually interacting with two external I^- anions, it is evident that the three I-I separations depend on the crystal environment with possible loss of the highest symmetry. Here, we present a simple model based on experimental and theoretical data, which highlights how the mixing of the key σ orbitals is affected by a different distribution of the positive charges in various crystals.[4] To determine the latter, the Hirshfeld surface approach has been applied to some selected experimental structures where the differences are most remarkable [5]. Systematic DFT calculations (in vacuum and solvent and) confirm that variously localized positive charges around the polyiodide can significantly affect the geometries of even the smallest I_3^- and I_4^{2-} units. The satisfactory results are interpreted in terms of a simple qualitative MO model, which monitors the σ orbital mixing for different positive charge distributions, hence the variable strength of the I-I bonding. The reciprocal validation between experiment and calculations and the predictability of the trends are the interpretational key to predict the variability of the halogen bonding in the smallest polyiodides and possibly in those of higher nuclearity.

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INO-PO-17 Catalytic membranes for indoor VOCs decomposition

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In indoor environments it is possible to detect different dangerous volatile organic compounds (VOCs). The most common VOCs grow from synthetic or semi-synthetic materials like plastic, wood composites and preservatives, foams insulation, furniture, flooring, paints and other solvents. One of the most dangerous and common indoor air pollutant is represented by formaldehyde that can be emitted from urea, melamine or phenol formaldehyde resins and from additives used for the wood treatment. The purification from formaldehyde and other VOCs of polluted air with a complete oxidation strategy is the final target of this project.

We are developing and testing a series of polymeric membranes containing catalytic species such as transition metal complexes able to promote the oxidation of VOCs using air's oxygen as oxidant.

Our membranes are obtained as polymer nanofiber webs by electrospinning technique (ES). The complexes choosen in the early step of the research are Cu and Fe complexes able to promote the formation of high reactive oxygen's species [1, 2]. The ES technique allows the dispersion of the metal complexes in the polymer solution before the ES process avoiding any further treatment of the membrane.

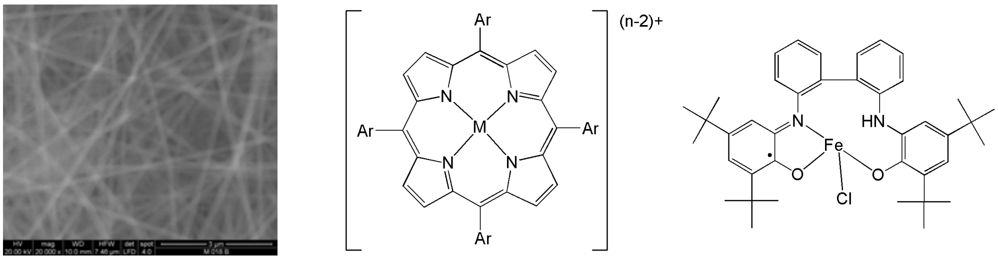

Figure 1. SEM image of a membrane and structure of some dispersed complexes

Aknowledgement. P. S., M. M. and M. R. wish to thank the Università degli studi di Padova (Progetto di Ricerca di Ateneo 2008 - CPDA083825) for the financial support.

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INO-PO-18 Water chemisorption on TiO_2 ultrathin films

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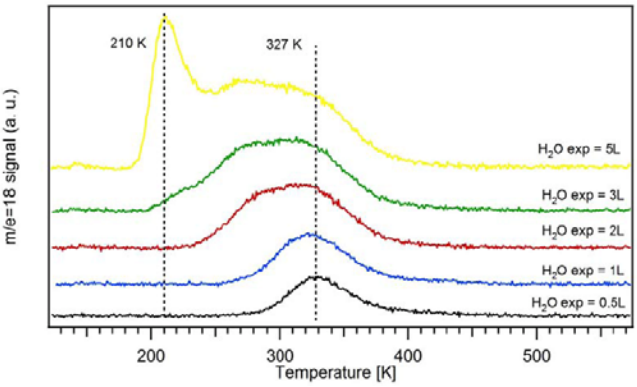
Ordered TiO_2 ultrathin films on Pt(111) surface can be prepared by reactive evaporation of Ti in a high-oxygen background [1]. Two rectangular phases, called *rect*-TiO_2 and *rect'*-TiO_2 can be obtained for Ti coverage up to 2 monolayer equivalent (ML_{eq}) (*rect*), and < 4ML (*rect'*), while for coverage > $4ML_{eq}$ TiO_2 grows forming the rutile $TiO_2(100)$ phase. All the phases were characterized by low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and photoemission measurements. These TiO_2 polymorphs form non-wetting layers on the Pt(111) surface and are characterized by incommensurate unit cells. The *rect*-TiO_2 corresponds to self-standing double layer with lepidocrocite-like structure, the *rect'*-TiO_2 has been assigned to TiO_2(B), while when the oxide thickness exceeds 40 Å the rutile phase appears to be the most stable one. We have then studied water chemisorption on these TiO_2 ultrathin films by Temperature Programmed Desorption (TPD) measurements (see for example Figure reported below). In order to verify the efficiency in the water dissociation process we have performed isotopic labeling experiments: the TiO_2 ultrathin films were grown using $^{18}O_2$ and the TPD measurements were performed by monitoring the peak corresponding to $H_2{}^{18}O$. This method allowed us to distinguish the water signal coming from the scrambling within the ionization chamber of the quadrupole from that actually caused by the water dissociation process on the surface, showing that the different TiO_2 polymorphs have different efficiencies in the dissociation process.



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INO-PO-19 Activity and deactivation pathways of penthamethyl-cyclopentadienyl-iridium molecular catalysts for water oxidation

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The green production of renewable fuels is one of the biggest challenges that scientists are currently facing. To overcome it, a significant contribution could derive from the efficient generation of molecular hydrogen through the catalytic splitting of water, driven by the sunlight. One of the bottlenecks of the entire process is the development of an efficient catalytic system for water oxidation to molecular oxygen.

Several coordination compounds of the transition metals were found to be competent catalysts for water oxidation. Furthermore, it has been recently showed that also organometallic compounds ($[Ir(ppy)_2(OH_2)_2]^+$[1], ppy=2-phenyl-pyridyne; $[IrCp^*L_1L_2(OH_2)]$,[2-6], Cp*= penthamethyl-cyclopentadieny) can be used as robust and fast catalysts for water oxidation.

All these catalysts, used in harsh acidic and oxidative conditions, undergo decomposition and it would be extremely important to evaluate which are the possible deactivation pathways and quantitatively contrast how the decomposition rate depend on the nature of the ancillary ligands.

In this contribution, we report on: (1) the performance of [IrCp*(ppy)Cl]Cl, $[IrCp^*(bzpy)NO_3]$ (bz=benzoyl-pyridine) and $[IrCp^*(H_2O)_3](NO_3)_2$ catalysts in terms of initial activity, long-term activity and TON (TurnOver Number); (2) *in situ* NMR studies aimed at intercepting possible intermediates and decomposition products; (3) DFT calculations on the mechanism of decomposition.

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INO-PO-20 Synthesis, NMR and theoretical study of Au(I) complexes with Nitrogen Heterocyclic Carbenes (NHC)

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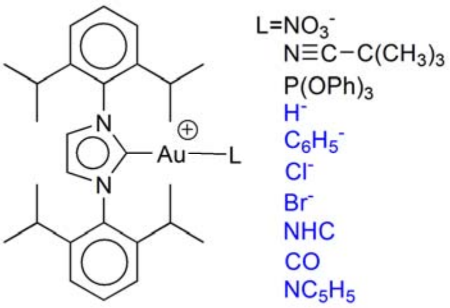
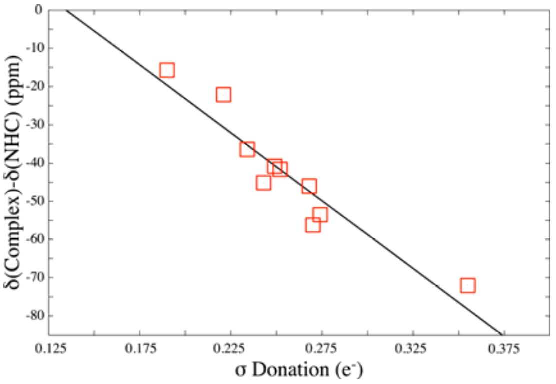
Linear compounds of gold (I) bearing NHCs as ancillary ligands find increasing application in chemistry [1]. Nevertheless, there is still some controversy on the basic aspects of the nature of the gold carbene bond, in particular regarding the relative weight of π-backdonation from the metal to the ligand and σ-donation from the carbene to the metal. Information about the nature of the carbene-gold bond can be obtained by evaluating the ^{13}C chemical shift of the carbenic carbon [2].

In this contribution we report: 1) the synthesis and NMR characterization of neutral and cationic NHC-Au-L compounds (scheme, L in black), 2) the theoretical determination of the chemical shift tensor of the carbenic carbon in a larger set of complexes (scheme, L in black and blue), and 3) the analysis of the charge displacement (CD) separated in terms of σ-donation and π-backdonation [3]. We found: 1) a rather good linear correlation between the chemical shift of the carbenic carbon and the donation component of CD (figure) and 2) that the π-backdonation component must be taken into account in order to correctly describe the gold-carbene bond since its contribution may approach up to 50% of the σ-donation. An analysis of CD and of the chemical shift tensor casts light on these findings.





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INO-PO-21 Novel cyclometallated Ru(II) and Ir(III) complexes as sensitizers for DSSCs

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In the last years research in the field of photovoltaic conversion and materials for solar panel is enormously increased for many fundamental reasons such as reduction of pollution, saving of energy cost and reduction of oil warehouse.

Solar cells based upon the semiconductor technology are at the present commercially available; their main disadvantages are the large energy amount required for the production of semiconductors and the rather high manufacturing cost. The main efforts in this field are therefore devoted to reduction of the costs and to an improvement of the efficiency of the solar cells.

In this framework, an important class of photovoltaic cells named DSSC (Dye-Sensitized Solar Cells) is extremely promising because it is made of low-cost materials and it is easy to produce.

The sensitizer is one of the key components, since it is responsible for the light harvest. It must exhibit excellent light harvesting properties and has to carry anchor groups to guarantee intimate contact with the semiconductor surface.

The pioneering and still one of the best sensitizer used for DSSCs is *cis*-dithiocyanatobis(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II) (N3).

However, recently cyclometallated Ru(II) complexes appeared as promising candidates for DSSCs, in particular due to their long term stability. [1, 2]

We synthesized and characterised novel cyclometallated Ru(II) and Ir(III) complexes which have been tested in DSSCs.

Details on these studies will be presented.

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INO-PO-22 Functionalized Shvo-Type Catalysts for Mild Upgrading of White Poplar Bio-oil.

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Shvo's diruthenium complex **1** is an active catalyst in a considerable number of homogeneous reactions.[1] Our studies on hydrogenation of bio-oil obtained from pyrolysis of white poplar demonstrated that **1** maintains its performances in spite of the complex chemical nature of the substrate leading to an almost quantitative conversion of the polar double bonds and promoting the hydrolysis of sugar oligomers into monomers.[2]

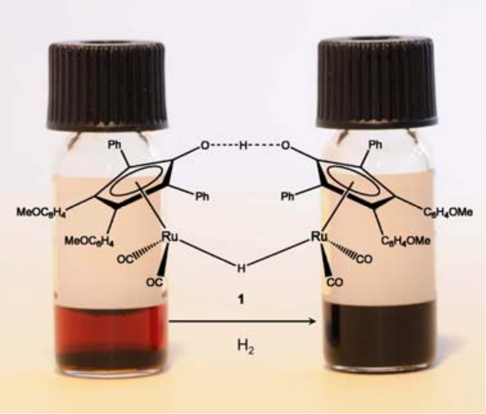

Figure 1**: Hydrogenation of white poplar bio-oil with Shvo catalyst **1

Recovery of the ruthenium catalyst remains the major problem which could be overcome by heterogenization. With the aim of immobilizing type **1** catalyst on insoluble support (*e.g.* silica, resins, hydrotalcites etc.) we investigated the synthesis of new –OH functionalized type **1** hydroxy-cyclopentadienyl-ruthenium-hydride $\{[3,4\text{-}(4\text{-R-C}_6\text{H}_4)_2\text{-}2,5\text{-Ph}_2(\eta^5\text{-C}_4\text{CO})]_2\text{H}\}\text{Ru}_2(\text{CO})_4(\mu\text{-H})$ (R= Br, $-\text{C}\equiv\text{CCR'}_2\text{OH}$; R' = H, Me, Ph) under both traditional and microwave assisted synthetic routes. Studies on iron analogues and their catalytic activity are also under investigation.

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INO-PO-23 New bis-guanidine Pt(II) complexes: synthesis and biological activity.

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The reactivity of organocyanamides (R_2N-C≡N, with R = alkyl) have been much less explored than that of organonitriles. Recently, the nucleophilic addition of ammonia to Pt(II)-coordinated organocyanamides has been reported to provide the bisguanidine Pt(II) compounds of the type *cis*- and *trans*-[$PtCl_2N(H)=C(NH_2)NR_2\}_2$)] (with R = alkyl) [1].
Our group investigated in the past years the addition reactions of primary (R'NH_2) and secondary (R'$_2$NH) amines to the C≡N triple bond of coordinated nitriles to afford the amidine complexes of the type *cis*- and *trans*-[$PtCl_2\{N(H)=C(NHR')R\}_2$] and *cis*- and *trans*-[$PtCl_2\{N(H)=C(NR')_2R\}_2$] [2] (with R = alkyl, aryl; R' = alkyl, cycloalkyl). Such derivatives demonstrated to possess a remarkable biological activity (both *in vitro* and *in vivo*) thus constituting a new generation of platinum antitumor drugs [3].
Here we describe the nucleophilic additions of dimethylamine to coordinated dimethylcyanamide to form new Pt(II) complexes (Figure 1) containing guanidine ligands $Me_2NC(NMe_2)=NH$.

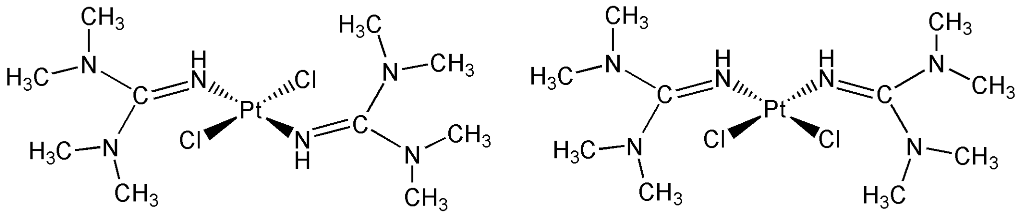

Figure 1. Structure of bis-guanidine Pt(II) complexes.

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INO-PO-24 Controlling quantum dot aggregation by acid/base switching

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Colloidal semiconductor nanocrystals have generated great interest in recent years for both fundamental science and technical applications [1]. Their main characteristic, which made them so popular, is the intense, narrow and size-dependent emission. Nevertheless, the achievement of good spectroscopic properties (high quantum yields, long term photostability) is strictly related to the quality of the material, particularly as far as surface states are concerned [2]. Indeed surface chemistry plays an important role in the manipulation of these materials, and is responsible of the sensitivity of the optical properties of quantum dots to the surrounding environment. In order to use inorganic semiconductor nanocrystals for sensing and biological applications, their response to changes in the environment must be known and understood. On one hand, it is necessary that the material is stable in a range of experimental conditions as wide as possible. On the other hand, the intrinsic sensitivity of the material to a specific analyte can be exploited for sensing applications, without the need of further functionalization of the surface [3].

In our study we focussed our investigation on the effect of acid and base on the properties of CdSe based core and core/shell quantum dots in organic solvent, comparing the same materials originating from different synthesis, materials with different organic ligands, and with different shell thicknesses. The surface of quantum dots is always covered by a shell of organic ligands, that prevent aggregation and passivate the surface of the nanoparticles. The acid competes with the nanocrystals for the ligands, which are Lewis bases, causing their detachment from the surface. As a consequence the nanocrystals aggregate and their luminescence is quenched. The process can be reversed by deprotonation of the ligands with a base.

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INO-PO-25 FROM P_4 TO $H_3P(O)$: UNPRECEDENTED PROCESS FEASIBLE VIA ELECTROCHEMISTRY

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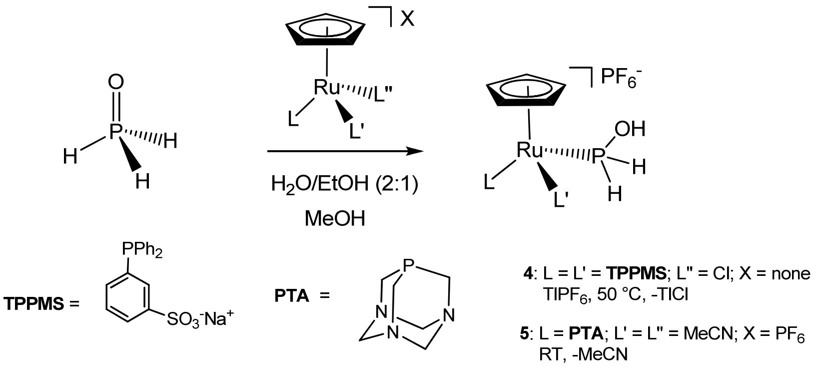
The elusive phosphine oxide has been observed for the first time in 1985 by Hamilton and Murrells,[1] who generated it by reacting O_2 with PH_3 using a discharge-flow system, and later on it was also obtained and trapped as a short-living species in solid argon matrices.[2] Herewith we report the preparation of the first defined compound bearing phosphorus with (-1) oxidation state, namely $H_3P(O)$, by electrochemical means using as starting material a suspension of white phosphorus in water and ethanol. The novel species has been generated through a stepwise process, involving first the reduction of P_4 to PH_3 and consequently its oxidation to phosphine oxide. Following tautomerization to phosphinous acid $H_2P(OH)$, $H_3P(O)$ has been trapped in the coordination sphere of ruthenium(II) moieties forming stable organometallic derivatives as shown in the scheme below.[3]



4: L = L' = **TPPMS**; L" = Cl; X = none
$TlPF_6$, 50 °C, -TlCl

5: L = **PTA**; L' = L" = MeCN; X = PF_6
RT, -MeCN

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COST Action CM0802 “PhoSciNet”, NATO(CPB.NR.NRCLG 983375), CNR-RAS bilateral agreement, PRIN 2007 are thanked for funding and Thermphos Int. (Vlissingen, NL) for a generous loan of P_4.

INO-PO-26 Cyclopropanation Reactions Catalyzed by Rhodium Porphyrin Bound to a Merrifield Resin

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The cyclopropyl ring is an important organic function due to the presence of such structure in a number of interesting natural products derivatives with antileukemic activity *in vitro*[1] . Several methods have been discovered in the past for obtaining such ring using copper, rhodium and osmium complexes as efficient catalysts for the synthesis of cyclopropanes from diazocompounds[2].

Synthetic iron, rhodium and osmium porphyrins have been also reported as catalysts for the cyclopropanation reaction of simple olefins by ethyldiazoacetate (EDA)[3]. Comparing with the simple copper catalysts, like CuCl which preferentially affords the *anti* isomers, the porphyrin catalysts give interesting results in reversing the *anti/syn* ratio of the products depending on the nature of the metal. The recycling of the catalyst without any tedious column separation, is an important goal in preparative chemistry because this fact allows to synthesize large amount of the products using small quantity of expensive metal complexes.

In this communication we will show the possibility to use an immobilized metalloporphyrin to catalyze the cyclopropanation of standard olefins with good yields and high *syn/anti* ratios compared with those obtained with normal metal compounds. The catalyst can be reused several time without any loss of activity.

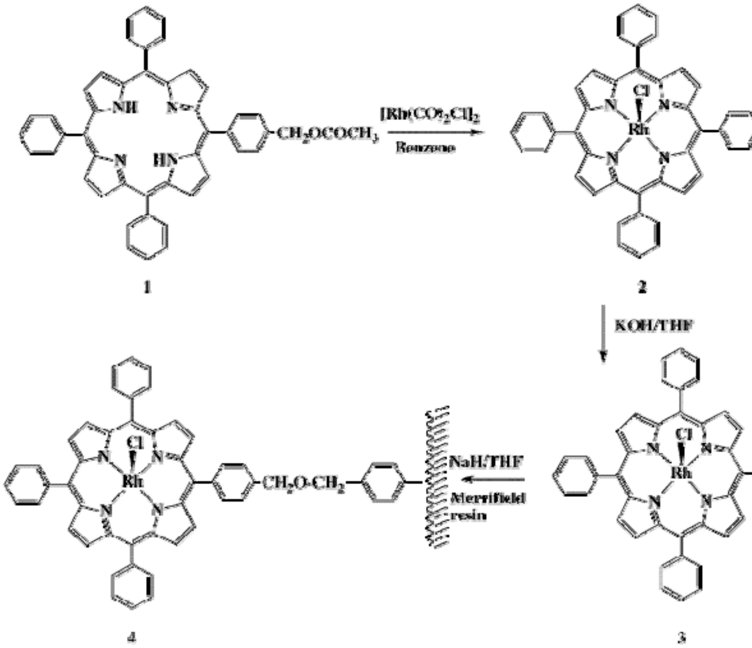

Fig. 1. Synthesis of the catalytic system

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INO-PO-27 New CPs Based on the Trinuclear Triangular SBU $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$ Connected through 4,4'-Bipyridine.

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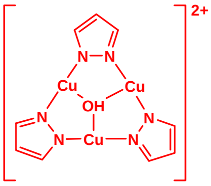
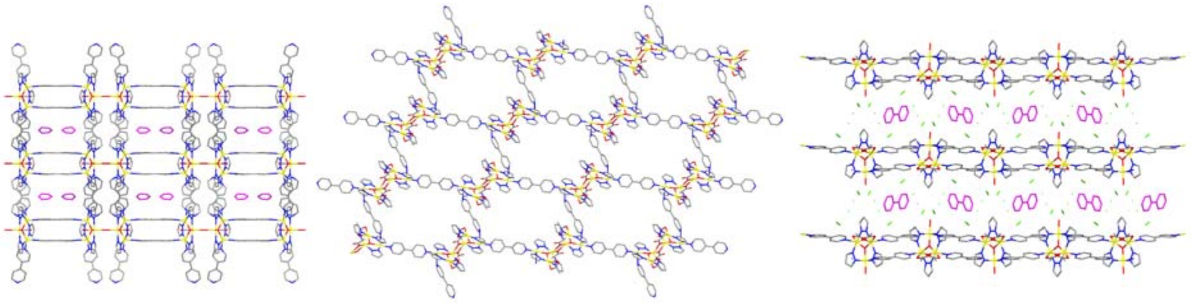
Coordination Polymers (CPs), often obtained by (self)-assembling oligonuclear metal clusters (the so-called Secondary Building Units or SBUs) are the subjects of a large and increasing number of studies due to their interesting properties and promising applications in numerous important fields, as gas storage, molecular recognition, catalysis, etc.[1] An important class of polynucleating ligands, useful to drive the self-assembly of CPs, is represented by donor units containing two 4-pyridyl moieties interconnected by various spacers, which can afford different lengths, linear or non-linear geometries, and conformationally rigid or flexible molecular skeletons.[2]

Recently, we developed a general procedure to obtain trinuclear triangular copper(II) complexes, having the $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$ core, (pz = pyrazolate) whose charge is balanced by two carboxylate ions.[3]



Continuing our ongoing research on the synthesis of new CPs, we treated $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(CH_3COO)_2(Hpz)(H_2O)]$ with 4,4'-bipyridine, obtaining new CPs, in which the trinuclear core is maintained.



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INO-PO-28 Dinuclear Pt(II)-bisphosphonates complexes: useful precursors of multinuclear or higher oxidation state platinum drugs.

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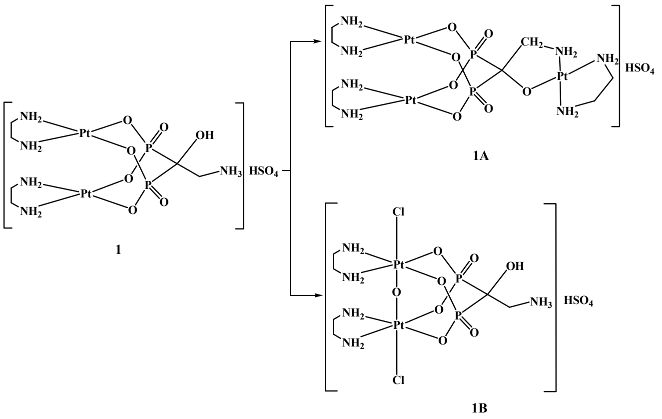
Cisplatin is one of the most successful drugs in cancer chemotherapy. Despite its success, treatment with cisplatin is limited by undesirable side effects[1].

The use of carrier ligands able to promote the specific accumulation of the drug in target organs or cells has been exploited as a strategy to overcome the side effects of cisplatin. In particular, geminal bisphosphonates (BPs), commercial drugs which show affinity for bones and other calcified tissues[2], have been used to promote the specific accumulation of platinum antitumor drugs in the bone with consequent significant improvement of the biological effect and reduction of the systemic toxicity. BPs are also aminable for the synthesis of polynuclear platinum complexes. The interest for the latter type of complexes has greatly increased in recent years thanks to their ability to overcome cisplatin resistance forming Pt-DNA adducts completely different from those of platinum drugs currently in clinical use.[3] Particularly, for mononuclear Pt complexes, has also been exploited their oxidation to Pt(IV) complexes which are much more inert to ligand substitution than their Pt(II) counterparts and are believed to undergo reduction to Pt(II) prior to reaction with DNA.[1]



1

1A

1B

In this work a dinuclear Pt(II) complex containing a geminal bisphosphonate (**1** in figure) has been used as a building block for the preparation of multinuclear (**1A**) or higher oxidation state (**1B**) platinum drugs.[4] The two new compounds have been fully characterized and their *in vitro* cytotoxicity has been evaluated.

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INO-PO-29 Effect of Si and Ge alloying addition on the electrochemical behaviour of Fe_3Al intermetallic compound

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Among all the intermetallic compounds susceptible to high temperature applications, iron aluminides have been attracting considerable attention for their applications as structural materials, owing to their high strength-density ratio, low row material cost and also good corrosion resistance, due to their ability to form a protective oxide layer. Many studies have been carried out on the oxidation behaviour [1,2] and on the tribological properties [3] of iron aluminides . However, to date, information concerning the corrosion behaviour in aqueous acid solutions of these compounds are scarce.
In this communication the influence of Si and Ge alloying addition on the electrochemical behaviour of Fe_3Al intermetallic compound in H_2SO_4 solution is assessed.
$Fe_{75}Al_{25}$, $Fe_{70}Al_{25}Si_5$ and $Fe_{70}Al_{25}Ge_5$ compounds were prepared by melting the stoichiometric amounts of pure elements in an arc furnace under a bit depression of argon. Light optical microscopy (LOM), scanning electronic microscopy (SEM), electron-probe microanalysis (EPMA) and X-ray powder diffraction (XRPD) were used to investigate the microstructure of samples. The electrochemical behaviour was assessed by means of polarization performed in aerated 0.25 M H_2SO_4 solution at room temperature (25 ± 0.1 °C). Potentiodynamic polarization curves were recorded in the potential range −800 ÷ +2000 mV/SCE (Saturated Calomel Electrode) at a scan rate of 1 mV/s. X-ray photoelectron spectroscopy (XPS) measurements were carried out on the samples surface after the electrochemical tests in order to gain information about the composition of surface layers. Preliminary results show a positive influence of silicon and germanium alloying addition on the passivity of Fe_3Al intermetallic compound.

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INO-PO-30 Acid–Base Interaction between Transition-Metal Hydrides: Dihydrogen Bonding and Dihydrogen Evolution

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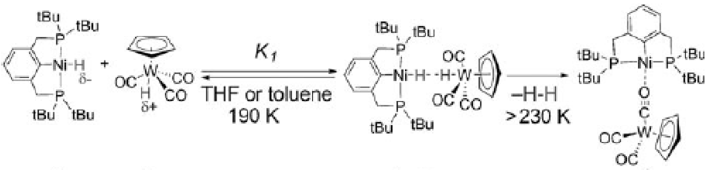
Unconventional hydrogen bonding that involves transition metal complexes has attracted considerable attention and several efforts have been made to rationalize the many conceivable interactions. However, dihydrogen bonding interactions where transition metal hydride complexes serve as both proton acceptor and proton donor in a hydrogen bond have not been described, although dihydrogen evolution was observed when "hydridic" and "acidic" hydride complexes are allowed to react. To further investigate this unconventional acid–base interaction, we report on the reaction of the stable electron-rich nickel(II) pincer hydride $[(2,6\text{-}C_6H_3(CH_2PtBu_2)_2)Ni(H)]$ (**1**) with the acidic tungsten(II) complex $[CpW(H)(CO)_3]$ (**2**).[1] Mixing equimolar amounts of **1** and **2** in carefully degassed THF at 273 K under a nitrogen atmosphere led to a reddish-orange compound, accompanied by H_2 evolution. Replacing **1** with $[(2,6\text{-}C_6H_3(CH_2PtBu_2)_2)Ni(D)]$ or **2** with [CpW(D)(CO)3] led to HD formation. Single crystal X-ray diffraction analysis revealed that the final product is the bimetallic ion pair $[CpW(CO)_2(\square\text{-k,C:k,O-CO})\cdots Ni[(2,6\text{-}C_6H_3(CH_2PtBu_2)_2)]$ (**3**).



1 **2** **1···2** **3**

By monitoring the process by multinuclear VT NMR, relaxation NMR studies and VT IR spectroscopy in the 190–298 K temperature range, strong experimental evidences have been obtained for the formation of a **1···2** adduct in which a NiH···HW unconventional hydrogen bond precedes the H_2 elimination that yields **3**.

Acknowledgements: The authors thank the projects "Firenze Hydrolab" (ECRF – Firenze), "PIRODE" (MATTM - Rome), the RFBR, project 11-03-01210 (Moscow), and the CNR-RAS bilateral agreement for supporting this research.

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INO-PO-31 Synthesis and Photophysic Properties of new Phosphorescent cyclometallated heteroleptic Iridium(III) phenylpyridinato Complexes

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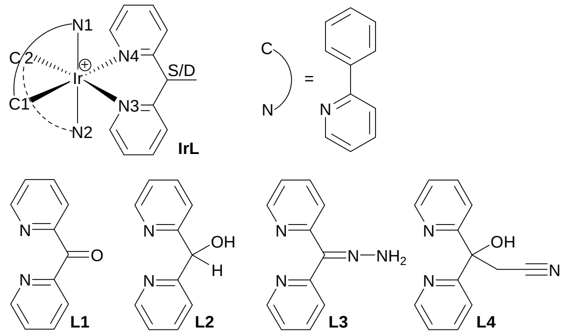
Luminescent iridium(III) complexes received increasing attention for outstanding luminescence properties such as high intensities, lifetimes in the μs time range, and emission wavelengths that can be tuned to cover a full range of visible colors, from blue to red..

However the synthesis of Ir(III) complexes by the preparation of the appropriate organic ligand followed by its reaction with the metal precursor cannot be performed whenever reactive units present in the ligand do not tolerate harsh synthetic conditions. In order to search an effective way of increasing the emission quantum yield at RT we synthesized new phosphorescent cyclometallated heteroleptic iridium(III) phenylpyridinato complexes $[Ir(ppy)_2(L)]^+$ (where ppy = phenylpyridine and L = bipyridine type ligand derived from di-2-pyridylketone) where the usual synthetic procedure of reacting the iridium dimer $[Ir(ppy)_2Cl]_2$ with an appropriate ligand (L) has been substituted by exploiting the reactivity of the carbonyl group of the $[Ir(ppy)_2$(2,2'-dipyridylketone)$]^+$ (**IrL1**) complex. The reduction of the carbonyl group with $NaBH_4$ on **IrL1** affords $[Ir(ppy)_2$(dipyridin-2-ylmethanol)$]^+$ **(IrL2),** whereas $[Ir(ppy)_2$(2,2'-(hydrazonomethylene)-dipyridine)$]^+$ **(IrL3)** and $[Ir(ppy)_2$(3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile)$]^+$ **(IrL4)** have been obtained by nucleophilic addition of hydrazine in methanol and potassium hydroxide in acetonitrile respectively. All the complexes were obtained in reasonable or almost quantitative yield and fully characterized.

It is worth noting that slight modification of the ketone moiety introduces relatively large changes in the photophysical behavior of the iridium complexes. TD-DFT studies were undertaken to rationalize the key role of the ketone group and its modifications to form non-conjugated cyclometallated ligands on the photophysical properties of these closely related iridium (III) complexes.



INO-PO-32 DFT and synchrotron-based X-ray studies of photoactivable complexes

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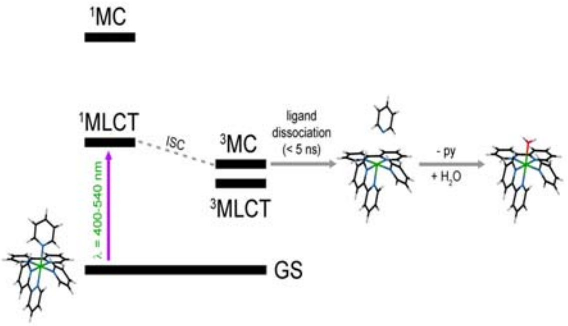
Selective activation of prodrugs can be achieved in cells using photoactivable metal complexes [1]. This class of derivatives offers unique possibilities for new applications in cancer therapy since light activation allows direct control of site, time and dosage of active species in tissues and organs. For example, light irradiation of metal complexes can trigger formation of reactive species and promote selective interaction between metal complexes and target macromolecules (DNA, proteins), which would not take place in the dark.

The study of the ground- and excited-state electronic structure of such derivatives is crucial for understanding the mechanism of action of these molecules and for the development of new anticancer agents with improved photophysical and photochemical properties. Hence, we are exploring the combined use of DFT and TD-DFT with time-resolved X-ray to gain insights into the electronic structure of photoactivable complexes and to capture the time dependence of their excited-state structural evolution.

Here we report a Time-Resolved Wide Angle X-ray Scattering (TR-WAXS) study on photoactive *cis*-$[Ru(bpy)_2(py)_2]Cl_2$. Upon excitation of its metal-to-ligand charge-transfer (^{1}MLCT) band centred at 460 nm, this model compound efficiently releases one pyridine ligand and subsequently coordinates a solvent molecule (H_2O). TR-WAXS allows direct observation of pyridine dissociation from *cis*-$[Ru(bpy)_2(py)_2]Cl_2$ in the 100 ps – 10 ns time-range. The transient structures captured by TR-WAXS were used to complement computational results and to validate DFT-optimized structures [2,3].



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INO-PO-33 Influence of the solvent in carboxylation and/or reduction of axial dihydroxo Pt(IV) complexes with *cis*-1,4-DACH as diamine ligand.

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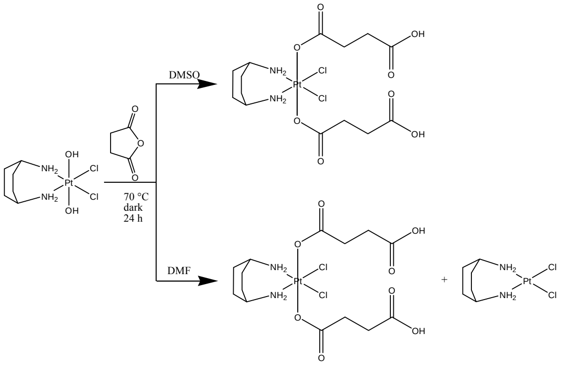
Pt(IV) complexes are seen as potential prodrugs able to be activated to the corresponding active Pt(II) complexes after reduction and loss of the two axial ligands. Pt(IV) complexes are more kinetically inert than the Pt(II) ones and hence can be orally administered. Moreover the presence of two extra ligands in the axial positions allows to tune some very important features such as solubility, lipophilicity and redox potential. Axial disuccinato complexes have an optimal redox potential compared to axial dichlorido complexes (too easily reduced) and axial dihydroxido complexes (too difficult to reduce)[1]. Moreover the presence of two free carboxylic functions allows their conjugation of active molecules which, after their release following the reduction process[2, 3], could improve the pharmaceutical effect. Starting from [$PtCl_2$(*cis*-1,4-DACH)] (DACH= diaminocyclohexane) [4, 5] we performed the synthesis of the axial disuccinato Pt(IV) derivative following a well known synthetic pathway which involves the preparation of the axial dihydroxido Pt(IV) complex and the following carboxylation using succinic anhydride. For cisplatin and other Pt(II) analogs the latter reaction is straightforward if performed in DMF. We have found that starting from *cis, cis, trans*-[$PtCl_2$(*cis*-1,4-DACH) $(OH)_2$] the carboxylation reaction in DMF leads to the desired product but there is also a side reaction leading to the reduced Pt(II) precursor. This behaviour, that is reduction in the absence of a specific reducing agent, is not reported in the literature [6]. Performing the reaction in DMSO we did not observe the formation of the reduced Pt(II) precursor. We have investigated the mechanism of the reduction reaction and the conditions that are crucial for the formation of the reduced species in the absence of specific reducing agents.



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INO-PO-34 Developing new di-iron containing proteins as catalysts for oxidation reactions

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The quantitative and high efficiency detection of several analytes is required in many different areas. Since the basic concept of enzymatic electrode by Clark and Lyons and after successful applications of glucose-oxidase based biosensors in blood glucose measurement [1], a bio-revolution in chemical analysis has been occurring. Recently, interest in organic pollutant biosensing has been growing [2]. In this regard, Toluene Monooxygenase family (TMOs), a four components bacterial multi-component monooxygenase, can be of crucial utility as it is able to hydroxylate a variety of organic compounds, such as halogen alkanes and aromatic derivatives, consuming equivalents of dioxygen or hydrogen peroxide. A cost/time effective alternative to the classic microbial biosensor [2,3] is the adoption of synthetic compounds able to mimic TMO activity, bypassing enzyme purification process and overtaking cell diffusion limits.

Full-organic ligands coordinating two metal centers, which are able to mimic enzyme reactivity [4], and, small peptides, which are able to fold into four-helix bundle motives [5], have been developed in the last decades. An interesting strategy is the synthesis of small peptide chains, with amino acid sequence containing information both for a proper folding and for metal binding. In the last years, several models of a di-metal self-assembling four-helix bundle motif has been obtained by means of *de novo design*, the DF series [5]. Recently, redox activity has been achieved with the di-iron DF3 model [6]. It is able to bind and successfully oxidize phenolic substrates, similar to the natural enzyme alternative oxidase. This result assures the suitability of DF-like scaffolds for engineering new catalytic site through various metals and coordination geometries. Here, we report the design and a preliminary computational study of new DF variants, mimicking TMO active site geometries and second shell interactions.

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INO-PO-35 Design and Preliminary Characterization of New Heme-Protein Models

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Mimochromes are a class of peptide-based heme-protein models, containing two α-helical peptide chains covalently linked to deuteroporphyrin IX [1]. They provide a remarkable opportunity to explore how both catalytic activity and stability of the heme cofactor are regulated by different and specific interactions with the protein matrix, ranging from coordinate and hydrogen bond, to hydrophobic and ionic interactions [2].

Here, we describe two new models, engineered on the Mimochrome IV crystal structure [3]. They are made up of two 17 residue peptides. Unlike the other members of the class, the peptide chains are elongated by 6 residues at the N-termini. This extra peptide segment, modeled in extended conformation, is intended to ensure further protection to the heme, thus increasing stability and specificity. To stabilize the desired protein folding, residues were chosen to give a large number of intra- and inter-chain interactions.

The first model contain two identical peptide chains, with a bis-His heme coordination. Preliminary CD and Uv-vis analysis confirmed the expected conformation and heme coordination. The ability of this symmetrical model to act as an electron-transfer protein is presently under course.

To mimic peroxidase-like activity [4], a second model was developed. The two peptide chains around the heme have different composition: one peptide chain houses the proximal histidine in a mainly hydrophobic environment; the second chain provides a cavity for binding small exogenous compounds and contains key residues for catalysis (Arg and His). The Uv-vis spectra of the un-symmetric model is typical of mono-His coordinated heme. The preliminary structural and functional characterization of these models will be presented.

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INO-PO-36 Electrostatic Interaction between Charged PMMA Core-Shell Nanospheres and Cytotoxic Platinum Complexes

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The drug targeting and delivery approach aims at reducing chemotherapy-related systemic side effects. Passive targeting is based on the use of natural or synthetic macromolecular vectors to exploit the “enhanced permeability and retention” effect (resulting from the low vascularity and abnormal morphology of tumor vasculature) in order to selectively deliver cytotoxic agents to tumor cells.

Previously, we employed positively charged polymethylmetacrylate (PMMA) core-shell nanospheres as vectors for the anionic $[PtCl_3(NH_3)]^-$ complex. The antitumor effect of the resulting adduct was assessed in C57BL/6 mice bearing B16 murine melanoma. When used at the corresponding maximum tolerated doses, the adduct proved to be more effective than cisplatin in inhibiting B16 tumor growth and its in vivo efficacy correlated with Pt-intratumor accumulation.

The interaction between nanospheres and complexes of reversed charge is now studied. For this purpose, two cationic platinum compounds and PMMA core-shell nanoparticles (Fig. 1) bearing anionic ($-SO_3^-$) arms are used to determine whether such particles might serve as drug carriers for positively charged antiproliferative Pt drugs. As expected, the formation constant of the adduct with a dication Pt complex is significantly higher than that of a monocation one. Moreover, the stability of both adducts depends on the ionic strength and surface charge density of competing cations in the medium. The stability of the conjugates and the consequent retention and release of the drug from the nanoparticles will thus depend on both blood and extracellular fluid composition.

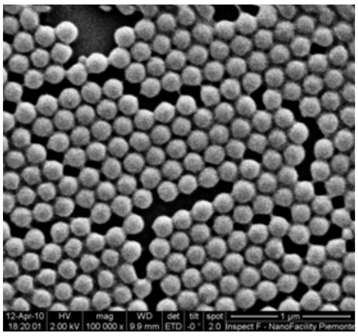

Figure 1.

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INO-PO-37 Gold Nanoparticles Functionalized with Artificial Metalloenzymes

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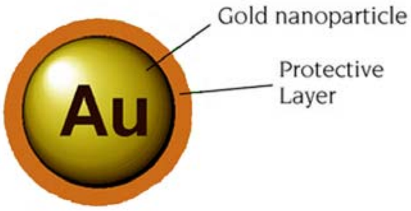
Nanoscience and nanotechnology are growing fields, which are gaining great impact in different areas, ranging from electronics and communication technologies to biomedical engineering. The production of nanomaterials, such as nanoparticles (NPs), is playing a central role. Due to their small dimension (1-100 nm), NPs exhibit properties that are often not observed in the bulk materials. For example, gold nanoparticles (AuNPs), the most stable metal nanoparticles, present unique electronic, magnetic and optical properties, and are experiencing applications in several fields, such as catalysis and biology [1,2,3]. The AuNP properties may be tuned, by controlling two key structural parameters: the size and the chemical nature of stabilizing ligand shell [2]. Therefore, the integration of nanoparticles with biomaterials, which display unique recognition, catalytic, and inhibition properties, may yield novel hybrid nanobiomaterials with synergic properties and functions [4].



In this contest, we are interested in developing biomolecule–nanoparticle hybrid systems, made up of AuNPs conjugated to artificial metalloenzymes [5,6]. In particular, artificial heme-proteins with peroxidase-like activity [7], have been conjugated to AuNPs, with the aim of exploring their potentials in the development of biosensors and immunosensig assays. The synthesis and the spectroscopic and functional characterization of the new nanobiomaterials will be presented.

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INO-PO-38 Ruthenium porphyrin-peptide conjugates: synthesis and characterization

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Early interest in the chemistry of ruthenium porphyrin systems was related to the use of metalloporphyrins as models of the cytochrome P450 and peroxidase enzymes, with respect to the oxidation of organic compounds. The close periodic relationship of iron and ruthenium suggests that ruthenium could represent a useful candidate for replacing the biologically significant iron, in iron-centered reactions. Further, ruthenium displays a rich coordination and redox chemistry, which spans oxidation states from +2 to +7 in the porphyrin ligand environment [1].

Nowadays, studies on ruthenium-porphyrin compounds expand and focus on diverse area of research that acknowledges not only their role as valuable biomimetic models, but also their potential for the development of suitable synthons in coordination and organometallic chemistry [2], building blocks for supra- or super-molecular assemblies [3], materials [4], and sensors [5]. The use of ruthenium-porphyrins in medicinal chemistry [6], as cancer terapeutics and photosensitizer in photodynamic therapy, is also receiving great interest.

In this perspective, our laboratory has developed a series of water-soluble ruthenium porphyrin-peptide conjugates, synthesized through the covalent attachment of peptides to the Ru(II)-deuteroporphyrin. They were designed to accommodate in their interior small ligands, based on the stability of ruthenium-small molecules (O_2, NO) complexes. Therefore, these new ruthenium complexes may represent attractive candidates in the construction of environmental and biomedical sensors.

Here, we report their synthesis and spectroscopic characterization, together with preliminary NO binding analysis.

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INO-PO-39 Synthetic transducers in affinity third generation electrochemical biosensors.

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A biosensor is an analytical device that relies on a biological recognition element, communicating with a signal transducer that provides a measurable response related to the concentration of the analyte. Electrochemical biosensors, which exploit an electron transfer (ET) event at a solid electrode for signal transduction, are the most promising biosensors, in terms of ease of construction, costs, versatility and miniaturization [1]. In particular, third generation biosensors exploit the direct electron transfer occurring between an electrode and a redox-active species immobilized onto it. The biological interaction is transduced into a current signal, thus resulting in an amperometric detection of the analyte [2].

Efficient direct ET reactions have been reported only for a restricted number of redox enzymes [3]; several studies based on heme-proteins adsorbed or immobilized on various electrodes showed that high-molecular weight enzymes are often not suitable for direct electrical communication with the electrode [4]. Our strategy to overcome these limitations is the use of artificial low-molecular weight proteins, designed on rational bases, to own the required activity [5]. We developed a class of covalent heme-peptide conjugate, named Mimochromes, with the aim of understanding the effects of the peptide chain composition and conformation in modulating the heme redox potential [6].

An affinity electrochemical immunosensor was developed using Mimochromes as redox tags for the detection of the binding events. The artificial ET protein, functionalized with a suitable recognition element, was covalently anchored on a gold electrode through self-assembled monolayers. The biosensor was characterized with voltammetric techniques and tested for analyte recognition.

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INO-PO-40 Synthetic metalloproteins for diagnostic applications

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Enzyme-linked immunosorbent assays (ELISA) are commonly used for the detection of analytes in biomedicine, food, and environment control. These tests are based on the formation of immunocomplexes, between an antigen and a specific antibody. The detector system is usually an enzyme (e.g. horseradish peroxidase, HRP), which is covalently bound to the antibodies. Immunocomplexes are quantified by measuring a colorimetric signal, deriving from the enzymatic reaction. The immunological component brings the detection specificity, while the enzyme component gives the analytical sensitivity [1]. The natural protein high dimensions provide quite low enzyme\antibody ratio, thus limiting the analytical sensitivity. The use of artificial, small metalloenzymes would represent an interesting solution, allowing a higher conjugation ratio and a considerable signal amplification. This approach will be crucial for the development of more sensitive immunochemical assays for the detection of very small amounts of analytes.

Herein, Fe^{III}–mimochrome VI is proposed as reporter enzyme for the functionalization of antibodies usable in ELISAs. Fe^{III}–mimochrome VI is a 3.5 kDa synthetic heme-protein model, which displays peroxidase-like activity, with a catalytic efficiency comparable to the native HRP [2,3]. Human polyclonal antibodies (hIgG) have been functionalized with this synthetic enzyme, by the use of cross-linkers. Conjugates with an enzyme/hIgG ratio up to 13 have been prepared. This represents a significant result, when compared to commercial immunoglobulins, which are usually linked to 3 - 4 HRP molecules. The complete characterization of the conjugates is in progress, in order to determine their immunoreactivity, as well as enzyme activity and structural stability.

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INO-PO-41 Which one among the Pt-containing anticancer drugs forms more easily monoadducts with *G* and *A* DNA bases? A comparative study between oxaliplatin, nedaplatin and carboplatin

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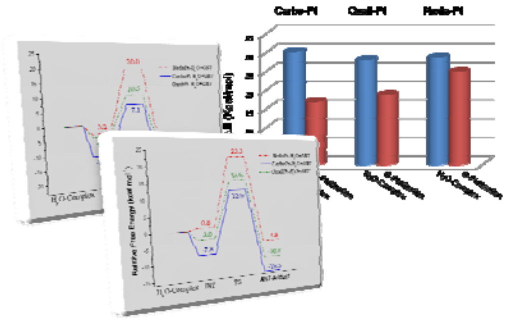
A good understanding of the interaction of platinum anticancer drugs with models of binding sites present in DNA is of fundamental importance to unravel the mode of action of this class of compounds.

In this work, the DNA bases platination processes of second- and third-generation Pt(II) anticancer drugs, have been investigated using Density Functional Theory (DFT) combined with the conductor-like dielectric continuum model (CPCM) approach, in order to describe their binding mechanisms and to obtain detailed data on the reaction energy profiles.

Although there is no doubt that a Pt-N7 bond forms during initial attack, the energetic profiles for the formation of the monofunctional adducts are not known.



Herein, a direct comparison between the rate of formation of CarboPt, NedaPt and OxaliPt adducts with Guanine ***(G)*** and Adenine ***(A)*** DNA bases has been made in order to spotlight possible common or different behaviour.

Together with previous works concerning the hydration mechanisms, [1] the goal of our work is to contribute to the elucidation of the whole mechanism employed by these compounds to reach the biological target.

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INO-PO-42 Investigation of Nanostructured Surface Conjugates with Non-conventional Thermal Analysis Coupled with FTIR and GCMS

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Thermal analysis (TA) is a well-known technique for materials characterization. The recent development of high-sensitive thermal balance has further increased the possibility of expanding thermogravimetric analysis (TGA) to surface features and surface-adsorbed moieties and which could be very promising in the field of the toxicity of mineral dusts. Furthermore, the possibility to analyse furnace gas with sensitive analytical techniques envisaged TA as a powerful tool to investigate complex surface conjugates. The recent in-line coupling of a high-sensitivity TGA with a FT-IR spectrophotometer equipped with a GC-MS dramatically expanded the application areas of the technique.

We report here about some non-conventional application of this innovative system devoted to the unveiling of the complex interactions between the surface of some inorganic nanoparticles and molecular compounds.

TiO_2 nanoparticles impregnated with alcohols or carboxylic acids (ethanol, ethylene glycol and citric acid) were subjected to TA in N_2 or O_2. Coupling thermograms (i.e. the sample weight loss as a function of temperature) with infrared thermograms (i.e. the integrated IR absorbance as a function of temperature) allowed us to discriminate between the weight loss due to water desorption and CO_2 formation subsequent to C-species oxidation. The temperature of desorption/oxidation of each molecular species was discussed in terms of conjugate stability.

The analysis of furnace gas was highly informative in two studies on the stability of pigments obtained by impregnation of sepiolite and palygorskite nanoclays with organic dyes, indigo blue and methyl red respectively. The interaction of the dye with the nanoclays structure was investigated by discriminating the dye desorption temperature from the hydroxyls condensation one. The study [1] indicated the degradation temperature of the pigment within the clay cages and the subsequent enhancement of the dye stability was demonstrated. Insights to the degradation molecular pathways of dyes were obtained.

The high specificity and overall versatility of the TGA-FTIR-GC-MS system in the characterization of complex inorganic conjugates is here showed with some relevant examples.

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INO-PO-43 *trans*-[Ru(PMe$_3$)$_2$(H$_2$O)$_4$]$^{2+}$ catalyzes H$_2$ production by selective decomposition of formic acid

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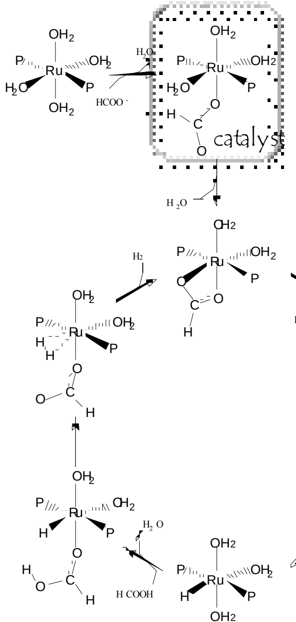
It is known that the reserves of fossil fuels are gradually decreasing and that the CO$_2$ emissions seem to be responsible for global warming [1]. The replacement of fossil fuels by sustainable energies has become essential for the future. To avoid the negative environmental impact of greenhouse gases, hydrogen has attracted increasing attention as an alternative secondary energy resource. However, the production and transportation of hydrogen in a cost effective, environmentally friendly manner is yet one of the major challenges to the development of the hydrogen economy.

An attractive alternative that can contribute to reduce CO$_2$ emissions is the use of CO$_2$ itself as a hydrogen carrier [2]. The combination of CO$_2$ reduction by H$_2$ in presence of an appropriate catalyst and selective decomposition of HCOOH to H$_2$ and CO$_2$ under mild conditions afford an environmentally benign system. The formation of H$_2$ by the catalytic decomposition of HCOOH has been the subject of many studies. As shown in a recent work, formic acid (HCOOH) decomposes selectively to afford H$_2$ and CO$_2$ in presence of a catalytic amount of a water-soluble, *trans*-[Ru(tppts)$_2$(H$_2$O)$_4$]$^{2+}$, ruthenium aqua complex, in a solution of HCOOH/HCOONa 9:1 [3]. A tentative catalytic cycle has been proposed by the authors on the basis of NMR experiments.

We have first investigated, by means of DFT, the mechanism (*Scheme*) proposed by the authors of HCOOH decomposition, catalyzed by *trans*-[Ru(PMe$_3$)$_2$(H$_2$O)$_4$]$^{2+}$. Next, we have explored other possible pathways that the reaction may follow, guided by computational evidences.



Scheme

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INO-PO-44 Investigation of the mechanism of reduction of *trans,trans,trans*-$[PtCl_2(CH_3COO)_2\{E\text{-}HN=C(CH_3)OCH_3\}_2]$.

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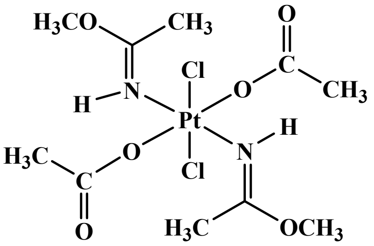

trans,trans,trans-$[PtCl_2(CH_3COO)_2\{E\text{-}HN=C(CH_3)OCH_3\}_2]$

The current search for platinum-based anticancer compounds aims at developing complexes which do not show cross-resistance with respect to the currently used platinum drugs or that can be taken orally.

Concerning the latter aspect, several Pt(IV) compounds have been proposed as antitumour drugs and one of them, satraplatin *cis*-$[PtCl_2(CH_3COO)_2(H_2N\text{-}C_6H_{11})(NH_3)]$, is in phase 3 clinical trial.

However, the reactivity of Pt(IV) complexes towards biologically relevant reducing agents, such as ascorbic acid and gluthatione, is not yet well understood preventing the rational design of new compounds with better pharmacological properties.[1] Among the limited number of investigations so far reported, we whish to mention that of L. I. Elding who studied the ascorbate reduction of JM216 and of its isomers [2] and the investigation of J. D. Ranford who explored the reduction of *cis,trans,cis*-$[PtCl_2(CH_3COO)_2(NH_3)_2]$ by methionine and cysteine.[3]

We have extended the investigation to *trans,trans,trans*-$[PtCl_2(CH_3COO)_2\{E\text{-}HN=C(CH_3)OCH_3\}_2]$ and studied its mechanism of reduction by ascorbic acid, glutathione, and triphenylphosphine using NMR spectroscopy, ESI-MS and electrochemical techniques.

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INO-PO-45 New Coordination Polymers from Cu^{II} Phthalate and Pyrazole

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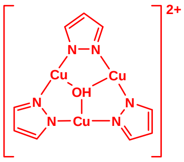
The studies on Coordination Polymers (CPs) [1] continue to produce a great number of publications, due not only to the intriguing "beautiful" structures often found in CPs, but also to their possible applications in different, important fields as catalysis, [2] gas storage, [3] etc.. On the other hand, it is not easy to predict *a priori* the results of the reactions of polytopic ligands with metal ions, to form CPs, avoiding a tedious trial-and-error approach.

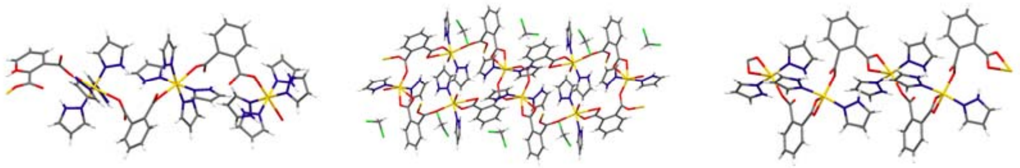
In the last years we deeply studied the interaction of Cu^{II} monocarboxylates with pyrazole (Hpz), generating mainly CPs based on the trinuclear triangular Secondary Building Unit [$Cu_3(\mu_3$-OH)$(pz)_3$], [4] (see Scheme).

$$3\,Cu(RCOO)_2 \;+\; n\,Hpz \;+\; m\,H_2O \xrightarrow{H_2O,\ MeOH\ or\ EtOH} [Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(RCOO)_2L_xL'_y] \;+\; 4\,RCOOH$$

L, L' = H_2O, MeOH, EtOH, Hpz



We are now studying and report here the results obtained in the reactions of Cu^{II} bicarboxylates with Hpz when different synthetic strategies were employed. Particularly, Cu^{II} phthalate was reacted with Hpz in different solvents, obtaining different CPs. The crystal structures of some of them are shown below.



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INO-PO-46 High Throughput Experimentation Studies on $MgCl_2$-Supported Ziegler-Natta Catalysts

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High Throughput Experimentation (HTE) technologies have profoundly innovated the research approach to olefin polymerization catalysts and polymerizations in major chemical companies (e.g., Dow, ExxonMobil, Borealis). In fact, the high complexity of these systems, in which subtle changes of catalyst formulation and/or application protocols may result into dramatic effects in performance, makes them ideal substrates for HTE. The huge potential of HTE for scientific and industrial purposes has been largely demonstrated, both for catalyst and process discovery [1,2].

Since 2006 our laboratory operates powerful HTE platforms for catalyst preparation and screening (*FreeSlate Core Module* and *FreeSlate PPR48,* respectively), housed into high performance glove-boxes and integrated with a large variety of on-line and off-line analytical techniques (es. NMR, ICP-OES, GC, LC, GPC, DSC).

As an example of practical application of these platforms to industrially relevant systems, in this poster we report on studies carried out on modern Ziegler-Natta catalyst systems for the production of isotactic polypropylene. As is well-known, such systems consist of a support ($MgCl_2$), a transition metal precursor (e.g. $TiCl_4$), an activator (e.g. an Al-trialkyl), and one or more electron donor modifiers (e.g. esters, ethers, alkoxysilanes) [3]. Until now, the extreme complexity of these formulations prevented a rational approach, and industrial research has been primarily empirical. In this poster, we demonstrate how a HTE approach can result into a 10x to 100x speed-up of structure/properties correlation studies, which is decisive for the implementation of models for mechanistic interpretations.

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INO-PO-47 Synthesis and Characterisation of Dinuclear N-heterocyclic Dicarbene Gold Complexes in (I-I), (I-III) and (III-III) Oxidation States

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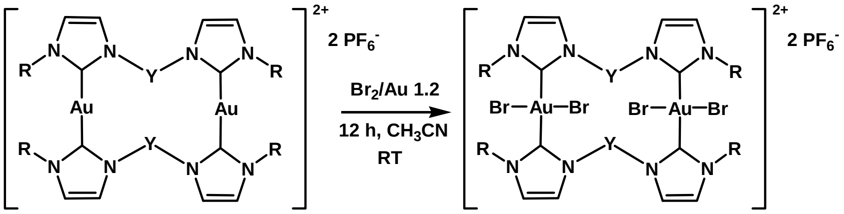
The research activity on the synthesis, characterisation and catalytic applications of N-heterocyclic carbene (NHC) complexes has been extended since few years to gold centers, as a consequence of the increasing interest in the chemistry of this metal [1]. Nevertheless, there are very few examples of gold complexes, bearing in the coordination sphere a dicarbene ligand [2].

In this contribution we report our recent results on the synthesis of novel dinuclear N-heterocyclic dicarbene gold(I) and gold(III) complexes, which are characterised by a dimeric structure with two dicarbene ligands bridging two metal centers.



The stability in solution of the various gold(III) complexes towards reductive elimination of Br$_2$ as well as towards structural rearrangement mostly depends on the flexibility of the bridging group connecting the two carbene units. Single crystals X-ray analysis indeed shows that this synthetic strategy affords dinuclear and polymeric bis-dicarbene Au(III)-Au(III), dinuclear mono-dicarbene Au(III)-Au(III), and, most notably, dinuclear bis-dicarbene Au(III)-Au(I) mixed valence complexes [3].

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INO-PO-48 Chain-Growth Versus Step-Growth: the Case of the Suzuki–Heck Polymerization between Fluorenyldibromides and Potassium Vinyl Trifluoroborate

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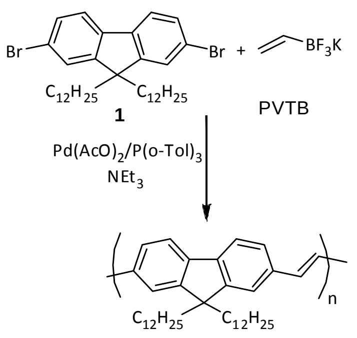
The mechanism of the Pd-catalysed Suzuki-Heck (*SuHe*) polymerization of 2,7-dibromo-9,9-di(*n*-dodecyl)fluorene (**1**) with potassium vinyltrifluoroborate (PVTB) for the synthesis of poly(fluorenylene-vinylene)s (PFVs) has been investigated. It was established that, in a first stage, a palladium catalyzed chain-growth AA/B(C)-type polycondensation occurs, as evidenced by the linear plot of the molecular weights of the forming polymer *vs* conversion. The chain-growth stage takes place until consumption of **1** and envisages the alternate addition of PVTB (by a Suzuki step) and **1** (by a Heck step) to the growing chain. Such alternate addition seems to proceeds via a peculiar catalyst transfer during which the metal is constantly bound to the growing chain and is corroborated by MALDI end group analysis. The second stage takes place by prolonging the reaction time after consumption of **1** and leads to the final polymer, that is formed by step-growth condensation of the fragments generated in the first stage (see Figure 1). With this mechanism operative, the molecular weights of the final PFVs depend on the PVTB/**1** feed ratio. Thus, using a PVTB/**1** molar ratio of 1.1 the final PFV was characterized by a M_n of 39600 Da whereas, using a PVTB/**1** molar ratio of 2.0, the final PFV was characterized by a M_n of 13200 Da.



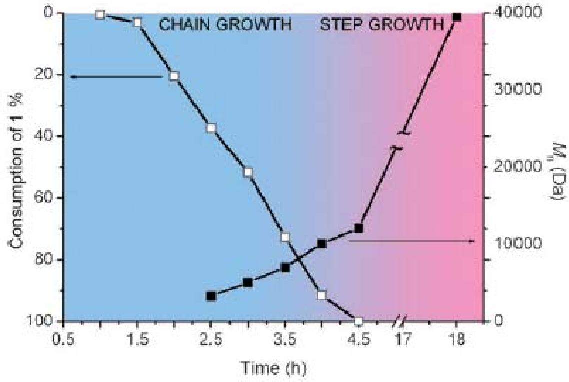


Figure 1. Consumption of **1** and M_n values of the polymer as functions of the reaction time for the *SuHe* polymerisation using a PVTB/**1** molar ratio of 1.1.

INO-PO-49 Functionalization of phosphazene systems with lipoic acid: synthesis, characterization and application.

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Phosphazenes are inorgano-organic materials with the general structure formed of -P=N- units, that may be cyclic or polymeric in nature. These materials showed both high synthetic versatility and good functionalization possibilities. Substituent groups used to prepare new types of cyclophosphazenes are mostly aliphatic and aromatic alcohols or amines commercially available in high quantities and low prices. [1] In our laboratories the synthesis of the 2,2-bis(4-oxazolinophenoxy)-4,4,6,6-bis[spyro(2',2"-dioxy-1',1"-biphenyl)]cyclotriphospha-zene (C-2-OXA) by reacting the corresponding cyclotriphosphazene containing two chlorine atoms, 2,2-dichloro-4,4,6,6-bis[spyro(2',2''-dioxy-1',1''-biphenyl)]cyclotriphosphazene (C-2-Cl), with 4-hydroxyphenyl-2-oxazoline has been previously optimized. [2] Here we describe the synthesis of a new type of cyclotriphosphazene obtained by reaction of C-2-OXA with lipoic acid (Figure 1). The study will be extended to hexa-substituted cyclo-phopshazene and to polymeric systems. Our purpose is to achieve not only a new material for metal coordination and abstraction but also new ligands for stabilization of metal nanoparticles. [3] The use of poly-functionalized ligands offers the advantage to achieve much stronger attachment to the nanoparticle surface to obtain more rigid structures susceptible of further modification.

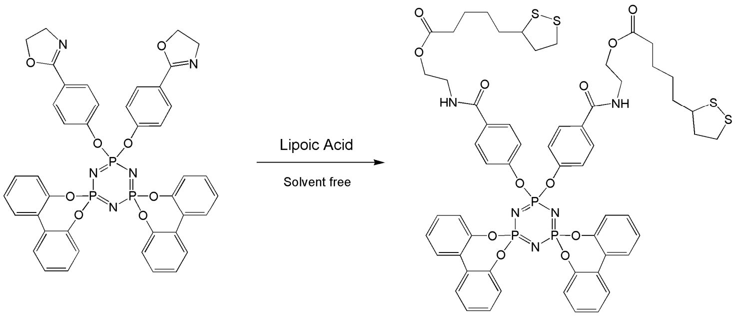

Figure 1. Synthesis of the lipoic acid derivative.

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INO-PO-50 Pt(II) complexes anchored on supramolecular aggregates labelled with Octreotide peptide.

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FDA recognized, more than thirty years ago, cis platinum based compounds for the treatment of a large number of solid tumors; anyway these drugs induce several side effects [1]. Many attempts have been carried out to reduce their toxicity and to prevent in-vivo inactivation. One of the most innovative approaches, is based on the encapsulation of the cytotoxic Pt(II) based drug in liposomes. A liposomal formulation may overcome platinum resistance by delivering a high dose of the drug at the tumor site. Stabilized PEGylated “*stealth*” liposomal formulations of cisplatinum have been developed in last decade [2]. These preparations exhibited an extended circulation time, increased anti-tumor efficacy and reduced toxicity compared to the free drug. In last years we developed peptide containing mixed aggregates able to deliver contrast agents and drugs to tumor cells overexpressing peptide receptors. The objective of present work is to formulate new aggregates able to carry new cytotoxic platinum complexes to cancer cells in a selective way. The new liposomal aggregates are obtained by co-assembling two amphiphilic monomers: a first monomer containing the octreotide bioactive peptide able to recognize somatostatin overexpressed receptors (SSTR2 and SSTR 5) and a hydrophobic tail based on two hydrocarbon chains with eighteen carbon atoms each (figure 1a). The second monomer contains the same lipophilic moiety and a lysine residue bearing on Nα and Nε amino functions an N-ethylglycine platinum complex and a PEG 1500 chain (figure 1b). The aggregates were characterized by dynamic light scattering (DLS) and SANS measurements. Both techniques indicate the presence of liposome.

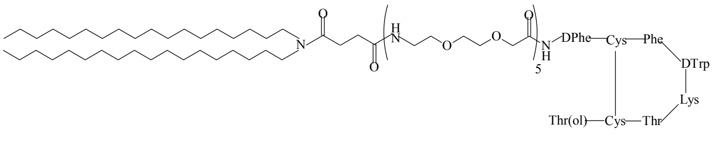

Figure 1a

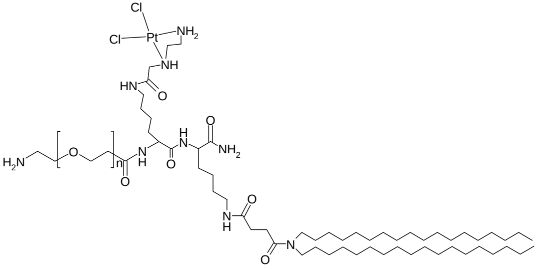

Figure 1b

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INO-PO-51 Mechanistic Study of Molecular Olefin Polymerization Catalysts: an Integrated Conventional and High Throughput Experimentation Approach

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Molecular catalysts for olefin polymerization are generally considered to be more easily amenable to mechanistic studies than heterogeneous ones, due to the well-defined structure of the precursors and a so-called ‘single-site’ nature [1]. This notwithstanding, discovering or even optimizing a catalyst by design is still a dream, because the number of physical and chemical variables which altogether determine catalytic behavior is simply too high. In fact, an initial phase of trial-and-error is still necessary, particularly in case of complex processes such as copolymerizations. In such a phase, the use of High Throughput Experimentation (HTE) tools and methods can be decisive for success [2].

In the present poster, we will explain how the integration of HTE with classical mechanistic methods can speed up the optimization of a new class of molecular catalysts for the industrial production of ethylene/propylene/diene (EPDM) terpolymers [3] by means of a high temperature solution process. Catalysts suited to this application must fulfill an impressive list of requisites, such as high thermal stability and polymer molecular weight capability, adequate copolymerization statistics, ability to incorporate the diene, etc.

In our laboratory, we operate since 2006 state-of-the-art HTE platforms for catalyst preparation and screening (*FreeSlate Core Module* and *FreeSlate PPR48,* respectively), housed into high performance glove-boxes [4]. Herein we will introduce an experimental HTE protocol for the fast generation of a structure/properties correlation database, that can be used as the starting point for the molecular kinetic modeling. The first conclusions of the mechanistic study of the aforementioned catalysts will be discussed as well.

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INO-PO-52 Which physico-chemical properties may be involved in silica pathogenicity?

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It is well known that occupational exposure to some crystalline silica polymorphs causes health damage. [1] In particular silicosis, the most ancient occupational disease, requires a close attention because of their invalidating consequences for a large number of workers and for a great number of benefits paid by the Italian government agency for the insurance against work-related injuries (INAIL).

In that regard, INAIL (Piedmont division) has funded a Ph. D fellowship in order to evaluate the number of cases of silicosis and lung cancer in Piedmont Region associated to the exposure to crystalline silica; to identify the most hazardous production divisions and to evaluate the physico-chemical properties of the silica dusts involved in the mechanism of pathogenicity. 444 cases of silicosis distributed in the Piedmont Region have been chosen and analyzed in detail. The analysis showed that 43% of the cases occurred in metallurgical activities, 26% to mineral processing, 15% to construction and 10% in other activities. Among all, 24 cases are associated with lung cancer. On the basis of the results obtained different samples selected from the most hazardous productive divisions and their physico-chemical properties wereinvestigated by means of different techniques including crystallinity (XRD), elemental analysis (XRF), micromorphology and particle size (SEM) were carried out for each sample. All samples were also tested for their potential to generate free radicals ($HO^{\bullet}$ and $COO^{\bullet -}$) (EPR/spin trapping) and for their surface charge. All samples contain quartz mixed to other crystalline phases, probably due to the presence of impurities, as shown by elemental analysis. All samples have a morphology and particle size typical of ground quartz and show a remarkable activity in free radical generation. The metallurgic division shows the highest cases of silicosis and their samples are the most reactive in the generation of free radical conferming a possible role of particle-free radical generation in the pathogenicity of crystalline silica. Further cellular studies will be required to support this hypothesis.

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INO-PO-53 Properties in solid and solution and cytoxicity of new thioureas palladium(II) complexes

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A new series of palladium(II) complexes of the type [Pd(N-N)(tu)$_2$]Cl$_2$ (N-N = 2,2'-dipyridyle or 1,10-phenanthroline; tu = thiourea, Et$_2$-tu, *n*-Bu$_2$-tu, *p*-tolyl-tu, Ph$_2$-tu) have been synthesized and characterized by elemental analysis and ^{1}H and ^{13}C NMR. [Pd(phen)(tu)$_2$]Cl$_2$ and [Pd(phen)(Et$_2$-tu)$_2$]Cl$_2$ have been also characterized in solid by X-ray analysis. This latter has shown that the coordination geometry of Pd(II) is perfectly planar and that distances and bond angles of the cationic fragment are in line with the corresponding structural parameters reported for analogous compounds. For both complexes, one of the two chlorides forms a strong interaction with two hydrogen atoms bound to nitrogen of the thioureas and the metal atom [1].

All the complexes are fairly soluble both in aqueous and in poor polar solvents. Their solutions in water are acidic and pH depends on the nature both of the thiourea and the bidentate ligand. The substances are very inert in solution. In particular, the electronic spectra of all the complexes, at fixed pH, do not vary in time for over a week, while they change with pH. Changes are fast and reversible, unless the pH is raised over about ten. Under these experimental conditions, a brown substance precipitates which in time turns black and becomes almost insoluble in any solvent.

The complexes with 2,2'-dipyridyle interact non-covalently with CT DNA, probably by intercalation [2]. When mixed with DNA, the analogous substrates with 1,10-phenantroline lead instead to precipitation of biopolimer fibres.

The complexes have been tested for in vitro cytotoxicity using cell line pneumocytes A549. Most of the complexes behave as cytotoxic agents comparable or stronger than cisplatin. Complexes with 2-2'-dipyridyle are less active than the analogous substrate with 1,10-phenantroline.

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INO-PO-54 New Phosphido Pincer Yttrium and Zinc Complexes as Efficient Catalysts for Ring Opening Polymerization and Copolymerization of Cyclic Esters

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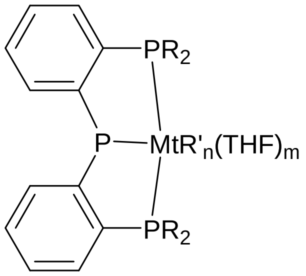
Aliphatic polyesters, such as poly(lactide), poly(ε-caprolactone) and their copolymers find a wide range of practical applications, from packaging[1] to more sophisticated biomedical devices.[2] The most convenient route to obtain polyesters with designed macromolecular architecture and controlled properties is the ring opening polymerization (ROP) of heterocyclic monomers initiated by metal complexes. In this context, rare-earth and zinc complexes are catalysts of particular interest because of their low toxicity, low cost, high reactivity and good control.[3-4]

Recently our group explored the use of tridentate phosphido-diphosphine ligands [(o-$C_6H_4PR_2)_2PH$; R = Ph or iPr] for the synthesis of new Groups 3 and 10 metal complexes (Figure 1) and their application as initiators for the ring opening polymerization and copolymerization of lactide and ε-caprolactone.

The yttrium complexes revealed to be very effective initiators for the ROP of ε-caprolactone and L-lactide under mild polymerization conditions showing activities among the highest ever reported in literature.[5] Immortal and living reactions were also feasible in presence of alcohol as chain transfer agent.[6] The zinc complexes showed moderate activities towards both monomers but uncommon abilities to copolymerize them to produce copolymers that were shown to possess monomer contents which correlated well with their composition in the monomer feed.



Mt = Sc, Y or Zn
R' = alkyl or amide
R = Ph, iPr

Figure 1

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INO-PO-55 Ruthenium complexes: versatility in supramolecular chemistry

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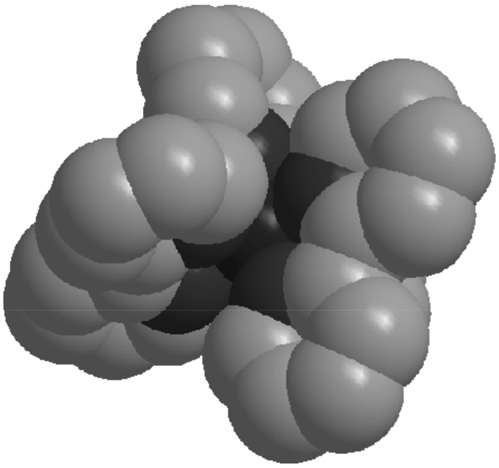

The photochemistry of ruthenium complexes has undergone an impressive growth in the last few decades.[1] Mostly in the last 15 years, Ru(II) polypyridine complexes have also contributed highly to the development of supramolecular photochemistry, and in particular to its aspects related to photoinduced electron and energy transfer processes within multicomponent (supramolecular) assemblies, including luminescent polynuclear metal complexes, light-active dendrimers, artificial light-harvesting antennae, photoinduced charge-separation devices, luminescent sensors, and light-powered molecular machines.

The assembly/disassembly of the luminescent dendritic hosts and the luminescent metal complex Ru(bpy)(CN)4]$^{2-}$,[2] photophysics of Ru^{2+} complexes containing terpyridine ligands appended with terthiophene units[3] and [Ru(bpy)3]$^{2+}$ as a 4-to-2 encoder and 2-to-4 decoder for molecular logic,[4] are three examples studied in our lab that demonstrate the versatility of these "old and well know" complexes in supramolecular chemistry.

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INO-PO-56 New coordination compounds containing nitrogen-rich ligands: synthesis, photophysics and electrochemistry

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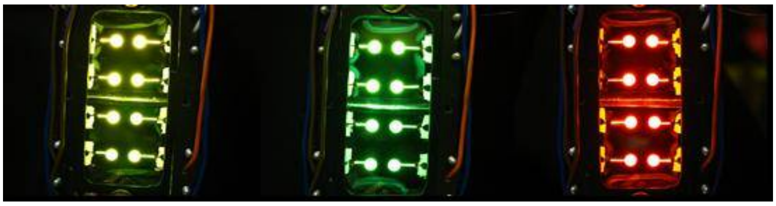
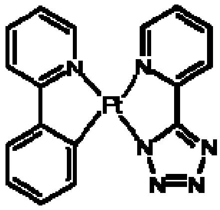
Tetrazolates, $[R\text{-}CN_4]^-$, were reported as excellent ligands for the construction of highly electrochemiluminescent Ru(II)-polypyridyl complexes and intensely emitting Ir(III)-cyclometalates.[1,2,3,4]

In particular, neutral Ir(III)-tetrazolate complexes have been used to fabricate a series of highly efficient OLED-type light emitting devices which displayed tunable emission colour as the consequence of slight modifications of the tetrazolate ligand structure.[5]. These promising results have driven our effort to the preparation of some new neutral Pt(II)- and Re(I)-tetrazolate complexes in order to construct new OLED type devices.

The research activity was also extended to the syntheses of eterobimetallic species; Ir(III)-Ru(II) and Ir(III)-Re(I), in wich the bridging tetrazolate ligand plays a key role in a energy transfer process. In addition, this class of ligands is also employed for the preparation of homo- and heteroleptic Cu(I)-tetrazolate compounds as new luminescent emitters for LEEC type devices.

The synthetic procedure, the photophysical properties together with the opto-electronic performances of all the new tetrazolate-based complexes will be discussed in detail.





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INO-PO-57 A RATIOMETRIC NANOSENSOR BASED ON FLUORESCENCE ANISOTROPY

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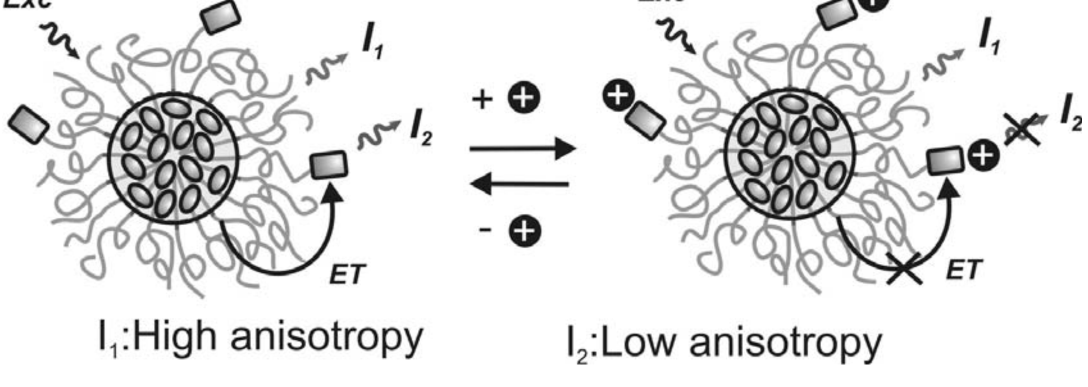
Silica Core-Surfactant shell nanoparticles (SCSS NPs) are versatile and effective platforms for the design of molecular based luminescent materials for energy conversion, imaging and diagnostics, signal processing and sensors.[1] The integration of a simple ON-OFF pH sensor (fluorescein) in SCSS NPs allows to achieve a very sophisticated ratiometric nanosensor (NS) based on dual detection of fluorescence anisotropy. In the NS a silica core, covalently doped with coumarine, behaves as an antenna system which transfers the excitation energy to the fluorescein molecules linked to the external surfactant chains. Energy transfer is not complete and the residual coumarin fluorescence (signal I_1) presents very high anisotropy since the rotational mobility of the molecules in the silica matrix is very low. The anisotropy of the sensitized fluorescence of the fluorescein, on the contrary, is vey low since the ET process causes depolarization (signal I_2). Protonation changes completely the photophysical properties of the fluorescein which, in the protonated form, is no more suitable to behave as an acceptor in the ET process; moreover its quantum yield is strongly reduced. As a consequence, protonation leads to a decrease of the fluorescence of fluorescein an to an increase of the signal of coumarin. In this modality the system hence behaves as a traditional ratiometric fluorescence sensor. As far as fluorescence anisotropy is concerned, its value in the 450-500 nm region (where emission is due only to coumarin: signal I_1) is independent on the pH. In the 500-600 nm region, on the other, hand fluorescence is the combination of I_1 and I_2 and the anisotropy is pH dependent. Fluorescence anisotropy at 480 nm can be hence used as a reference signal and the value at 520 nm analysed to determine the pH. Thanks to the combination of fluorescence anisotropy and multiple detection the NS has several advantages with respect to traditional chemosensors especially as far as elimination of background fluorescence is concerned. Finally the synthetic approach is very versatile and almost any kind of molecular sensor can be integrated in the nanostructure.



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INO-PO-58 Synthesis and characterization of new Ir_4 carbonyl clusters - phosphane ligands complexes.

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The chemistry of $[Ir_4(CO)_{12}]$ and its phosphane substituted products has been widely investigated with particular attention to the substitution kinetics and ligands distribution about the metal cluster.[1]
The neutral tetrairidium cluster and its derivatives are studied as they can find applications in homogeneous or heterogeneous catalysis, particularly in water gas shift and hydrogenation reactions. [2]

We have recently explored the reactivity of $[Ir_4(CO)_{12}]$ and $[Ir_4X(CO)_{11}]^-$ (X=Br, I) towards different types of polyphosphanes. This approach allowed us to aggregate several metal carbonyl clusters in order to get coordination polymers as well as discrete materials. Moreover we are developing a "library" of compounds with a potential catalytic activity.

Syntheses, X-ray structures and characterization of some dimeric mono- or three-substituted Ir_4 phosphane derivatives are here reported (**Fig. 1**).

In some cases, solvothermal approach has been fundamental in order to obtain single crystals, as only microcrystalline powders were available by traditional methods.

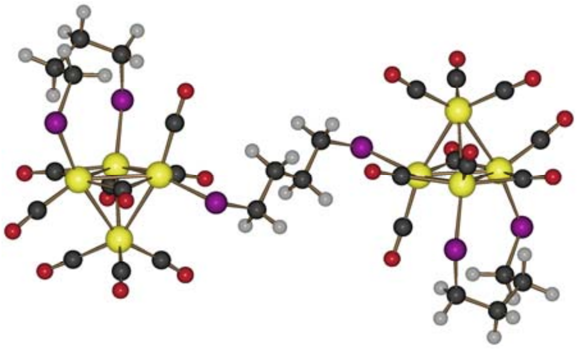

Fig. 1 X-ray structure of $[\{Ir_4(CO)_9(\mu\text{-dppbut})\}_2(\text{dppbut})]$. Phenyls on P atoms are omitted for clarity.

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INO-PO-59 Bifunctional Ethacrynic Acid – Pt Conjugates: *In vitro* Treatment of Malignant Pleural Mesothelioma.

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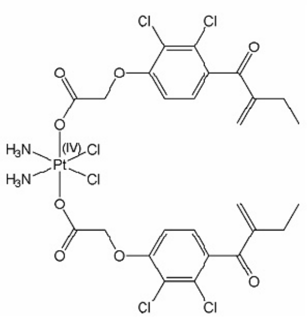
Malignant pleural mesothelioma (MPM) is a rare and aggressive asbestos-related cancer associated with poor prognosis. MPM cells are characterized by strong chemoresistance, often linked to the simultaneous induction of multiple antioxidant enzymes as the family of glutathione-S-transferase (GST).[1] Therefore, GST inhibition could be a adjuvant therapeutic strategy for MPM treated with Pt compounds. Ethacrynic acid (EA), a diuretic in clinical use, has been extensively tested and found to inhibit GST-family.[2]. In the present work, it has been realized the combination of EA and $[Pt(NH_3)_2]$ in a single, bi-functional cisplatin like compound, namely *cis*-[diamminodiethacrynatoplatinum(II)], **1**. Also its analogue Pt (IV)-based complex i.e. *cis*-[diamminodichloridodiethacrynatoplatinum (II)], **2** has been sinthesized. The cytotoxic effects of **1** and **2,** together with the combinations of cisplatin with two equivalent of EA have been tested on mesothelioma cell lines (having both epitelial or sarcomatous phenothype) and on a cisplatin-resistant sub-line. The biological results are reported.



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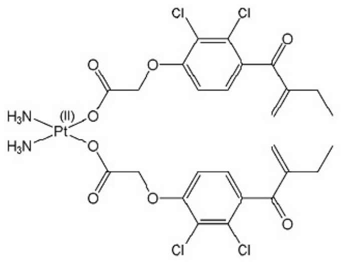

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INO-PO-60 Polymorphism and unusual bonding properties of dimeric Pt^{II}-pyrophosphato coordination complexes

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Isostructural, 'clamshell'-like, neutral dimeric pyrophosphato complexes of general formula $\{[M(bipy)]_2(\mu\text{-}P_2O_7)\}$ [M= Pd^{II} (**1**) or Pt^{II} (**2**)] were synthesized and studied through single-crystal X-ray diffraction, IR, ^{31}P NMR spectroscopy, and MALDI-Tof mass spectrometry.[1] Both complexes crystallize in the monoclinic chiral space group *Cc* as hexahydrates, $\mathbf{1}\cdot 6H_2O$ (**1a**, yellow crystals) and $\mathbf{2}\cdot 6H_2O$ (**2a**, orange crystals), and exhibit a zig-zag chain-like supramolecular packing arrangement with short and long intra-/inter-molecular metal-metal distances. A second crystalline phase of the Pt species was also isolated, with formula $\mathbf{2}\cdot 3.5H_2O$ (**2b**, deep green crystals), characterized by a dimer-of-dimers (*pseudo*-tetramer) structural sub-motif. Green crystals of **2b** could be irreversibly converted to the orange form **2a** by exposure to air or water, without retention of crystallinity, while a partial, reversible crystal-to-crystal transformation occurred when **2a** was dried *in vacuo* (Figure 1). ^{31}P NMR spectra recorded for both **1** and **2** at various pHs revealed the occurrence of a fluxional protonated/deprotonated system in solution, which was interpreted as being comprised, in the protonated form, of $[HO{=}PO_3]^+$ (P_α) and $O{=}PO_3$ (P_β) pyrophosphate subunits. **1** and **2** exhibited two successive one-electron oxidations, mostly irreversible in nature; however, a dependence upon pH was observed for **1**, with oxidation only occurring in strongly basic conditions. Density functional theory and atoms in molecules analyses showed that a d^8-d^8 interaction is present in **1** and **2**. In both cases, the HOMO is a weakly antibonding dσ^* orbital while the LUMO is a ligand-centered orbital. These unusual results suggest d^8-d^8 species can fall into two distinct categories. Category (i) comprises the majority of the known Pt^{II}, Rh^{I} and Ir^{I} dimeric species, in which the LUMO is a weakly metal-metal bonding orbital and the M-M bond order increases of 1 upon excitation. Category (ii) comprises species as all the known Pd^{II} dimers and compounds **1** and **2**, for which the LUMO is a ligand-centered orbital so that, upon excitation, the M-M bond order only increases of 0.5. To the best of our knowledge, **2** is the first example of a Pt^{II} system belonging to category (ii).

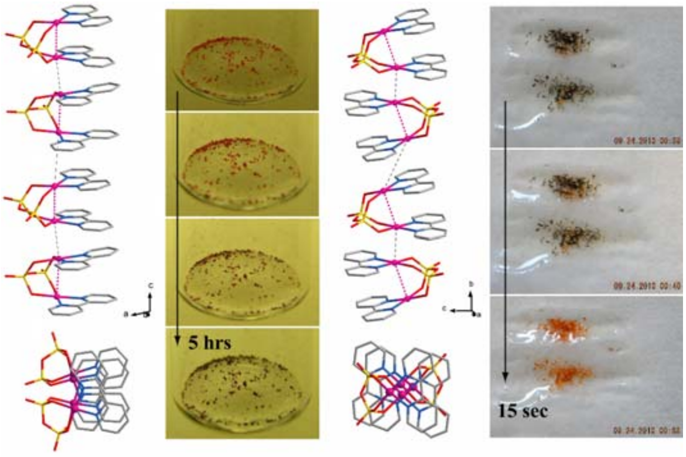

Figure 1.

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INO-PO-61 Ring Closing Metathesis Reactions Promoted by Ru-Catalysts with a *Syn* Substituted N-Heterocyclic Carbene Backbone

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Ruthenium-catalyzed olefin metathesis represents one of the most effective tools for constructing carbon-carbon double bond [1]. The development and improvement of metathesis transformations are essentially dependent on modification of catalyst structure.

Recently, we focused on the preparation of ruthenium complexes bearing *syn* and *anti* methyl substituents on the N-heterocyclic carbene (NHC) backbone and *o*-tolyl groups at the nitrogen atoms of the NHC ring [2]. These catalysts showed high efficiency in Ring Closing Metathesis (RCM) reactions and the *syn* isomers, in particular, revealed among the most active catalysts known in the RCM of hindered olefins up to now.

Herein we report the performances in RCM reactions of catalysts with a *syn* substituted NHC backbone presenting differently encumbered groups both at the *ortho*- position of the N-aryl rings (R in Fig. 1) and on the NHC backbone (R' in Fig. 1). The role of R and R' substituents on the catalytic behavior has been rationalized by investigating the RCM of different sterically hindered olefins with DFT calculations.

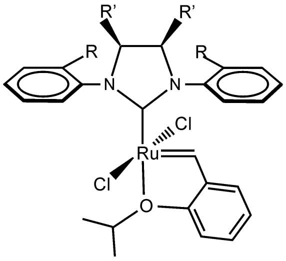

Figure 1.

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INO-PO-62 Copper(II) chiral complexes as components of cholesteric liquid crystals for optical applications

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It is known that chiral compounds mixed with nematic liquid crystals (LC), also commercially available such as TN0623, E7, etc., can generate a chiral liquid crystalline phase, called cholesteric (Ch) [1]. The phase arrangement is characterized by stacked nematic planes whose director gradually rotates on passing from one plane to the other, leading to macroscopic helicalization of the phase. Obviously two possible handednesses are expected, as a consequence of the use of *d* or *l* compounds. When a Ch LC is spread between two parallel surfaces, for example two glass slides, the helix axis spontaneously arranges perpendicularly to the surface of the so formed cell and the mixture generally appears uniformly distributed and optically homogeneous. An incident polychromatic unpolarized radiation can interact with the Ch phase giving rise to interference and reflection of a wavelength band $\Delta\lambda=p\Delta n$ (p=helical pitch, Δn=birefringence), so the mixture could appear colored by using radiation in the visible spectrum. Here we report on the use of copper(II) complexes with optically active (*d* and *l*) bidentate salicylaldiminate ligands, mixed with commercially available nematic LC. The main features of these copper(II) complexes are: the easy and inexpensive synthesis of both the *d* and *l* isomers; the marked thermal, chemical and especially photochemical stability (i.e., resistence to solar radiation); the very high compatibility with the host nematic LC (relevant for possible applications); high solubility in the LC phase also at lower temperatures; strong helicalization properties, that is a low weight percentage of chiral complex can produce a Ch phase with very short helical pitch. As an example, with about 10 wt% of our chiral complex a cholesteric phase with 450 nm helical pitch can be obtained, that is red light is reflected by the layer. The properties and potential applications of these compounds will be presented and discussed.

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INO-PO-63 New material from renewable resourses: Polysilicate-Lignin Composites

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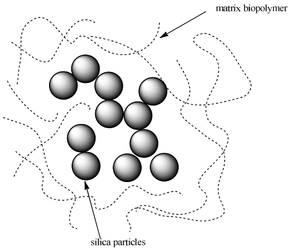
In the last decade Organic-Inorganic porous composite material -in nano or microscale- have been extensively studied since they combine advantages of inorganic materials (e.g. rigidity, thermal stability, inertiness) and the organic-polymeric phase (e.g. ductility and processability).

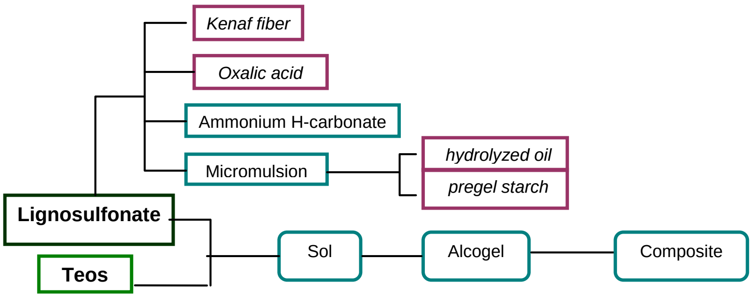
A defining feature of blended polymer composites, is that the dimension of the silica fillers[1] confers a dramatic increase in interfacial area, which may induce intrinsic crosslinking in the bulk. One of the most efficient procedure is colloidal sol-gel processes in the presence of a preformed polymer or monomers with tailored morfologies[2].

Herein we describe the formation of a new ecocompatible insulating material, adopting an hybrid procedure by using the **lignosulfonate,** as it is or subjected to thermal basic treatements (NaOH or NH_3), to provide partial depolymerisation.

The oligomers obtained can be dispersed, upon neutralization, in the **silica** colloidal mixture (TEOS aerogel) and furtherly polymerised in situ by adding a controlled amount of opportune **hydrophobising** additive (starch-oil biopolymer), **pH-moderator and expanding** reactants (NH_4HCO_3 and $H_2C_2O_4$). Ultimately, kenaf fibres (***Hibiscus cannabinus)*** were minced and finely dispersed as reinforcing agent.

Globally, the system is a natural rigid foam mainly composed by blended biopolymer/mesoporous silica. The porous microcomposite material obtained exhibits promising requirements of low density (0.5-0.2 g/cm^3) and low conductivity, adaptable for insulating uses in building application (bored-brick filler or small insulating panel). Preliminary results indicate the feasibility for a crosslinking process of lignin oligomeric chains with silanol and/or siloxane functionalities.





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INO-PO-64 Increasing the Maximum Nuclearity of Homometallic Rhodium Carbonyl Clusters by Interpenetration of Icosahedral Rh Moieties

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High-nuclearity transition-metal carbonyl clusters have always been regarded as chunks of metal lattices in a shell of carbonyl ligands. For instance, the homometallic Rh, Ir, Pt and bimetallic Ni-Pd and Ni-Pt carbonyl clusters systematically display close-packed metal frameworks. [1] In contrast, phosphine-substituted carbonyl clusters of Pd and Ni-Pd, as well as Au thiolate clusters, have a propensity for condensed, fused or interpenetrating centred icosahedral frameworks. [2,3]

We here report the isolation and structural characterization of the new $Rh_{26}(CO)_{29}(CH_3CN)_{11}$ and $[Rh_{33}(CO)_{47}]^{5-}$ clusters (see Figure 1). The latter raises the maximum nuclearity of Rh clusters, viz. $[Rh_{28}N_4(CO)_{41}H_x]^{4-}$. [4] Moreover, they both possess unprecedented frameworks based on interpenetrated Rh-centred icosahedral moieties. [5]

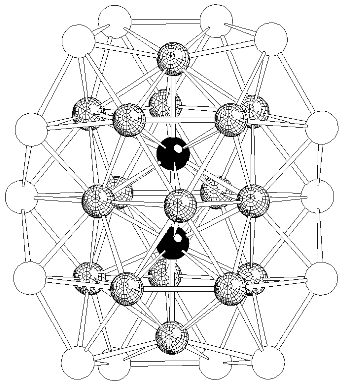

Figure 1. Metal skeleton of $[Rh_{33}(CO)_{47}]^{5-}$

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INO-PO-65 Copper(I) complexes and their application dye sensitized solar cells

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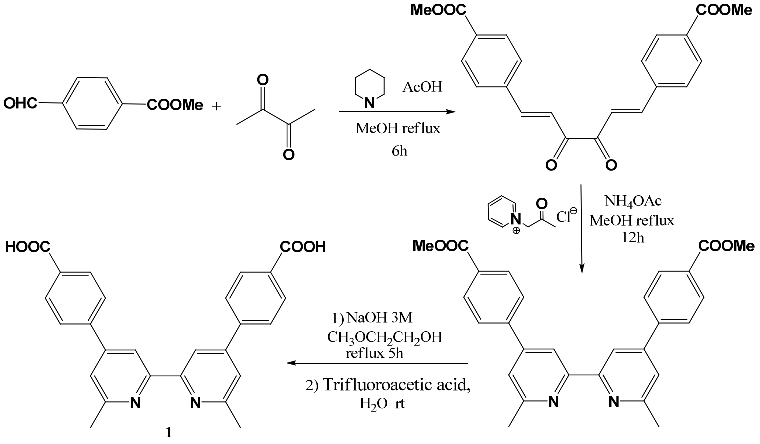
The easy prevision that in the near future the price of the energy derived from fossil fuels could be significantly increased and the well note limits in the applications of silicon-based photovoltaic (PV), get to the conclusion that the development of new, efficient and low-cost PV technologies will be more and more required. Up to day dye sensitized solar cells (DSSCs) represent one of the more attractive technological alternative to silicon-based PV. In this context, the best efficiency for the conversion of solar energy has been realized using a large number of Ru(II) polypyridyl complexes [1], however very good results were also obtained in the presence of metal-free organic dyes [2]. Recently also Cu(I) complexes have been proposed as effective sensitizers in DSSCs [3] even if their efficiency is much lower than that obtained with Ru-based devices, nevertheless copper still remains very interesting in this application because it can offer a considerable opportunity for reduction in cost.

Here we report the synthesis of suitable substituted 2,2'-dipyridil (Scheme 1) together with the corresponding bis-dipy Cu(I) complex.



Scheme 1

Several DSSCs devices have been prepared employing Cu(I) complexes with different protonation degree of the ligand **1**, and the results have been discussed as a function of the variation of the electrolyte.

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INO-PO-66 Reactivity of analogues of Zeise's anion with different ligands *trans* to the η^2-ethene

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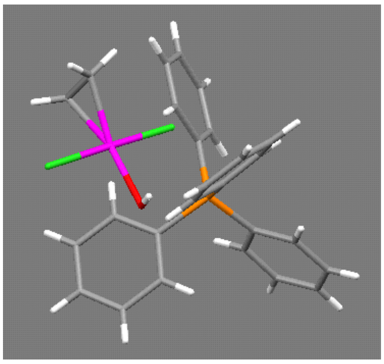
The Zeise's salt, K[$PtCl_3(\eta^2-C_2H_4)$], is a paradigmatic example of the olefin to metal bond [1] and still an important starting material for the synthesis of platinum-based organometallic compounds. The great reactivity of Zeise's anion, essentially related to the lability of the chlorido ligand *trans* to the olefin [2], which can be easily substituted by any ligand having a reasonable affinity for platinum.

To get further insights in the reaction of nucleophilic substitution upon changing the ligand *trans* to the η^2-olefin, we tested the reactivity of three monoanionic platinum(II) substrates (Zeise's anion itself, $[PtCl_3(\eta^2-C_2H_4)]^-$, **1**, *trans*-$[PtCl_2(OH)(\eta^2-C_2H_4)]^-$, **2**, and *trans*-$[PtCl_2(\eta^1-CH_2NO_2)(\eta^2-C_2H_4)]^-$, **3**), towards aromatic imines with different steric requirements (pyridine, 4-methylpyridine, and 2,6-dimethylpyridine). We also performed a *X*-ray crystal structure characterization of the tetraphenylphosphonium salts of **2** (see Figure) and **3**. Our data have highlighted the nature of the Pt-Cl Pt-OH, and Pt-C σ bonds. Cl^- is the only one of the three *trans*-to-olefin ligands which can have a π-acceptor capacity towards the metal. The σ-donor capacity of the ligands can be ranked in the order: $CH_2NO_2^- \gg Cl^- > OH^-$. The carbanion has an unexpectedly high weakening effect on the bond between platinum and the *trans*-olefin. As a consequence the olefin is displaced in preference not only by another olefin but also by σ-donors such as pyridines. In the light of the present results, the series ranking the *trans*-effect, which were set up in the 1980's [3], needs to be reconsidered in view of the importance for synthetic chemistry of *trans*-directing ligands.



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INO-PO-67 Reactivity behaviour of a Manganese(V)–Oxo Porphyrin Complex

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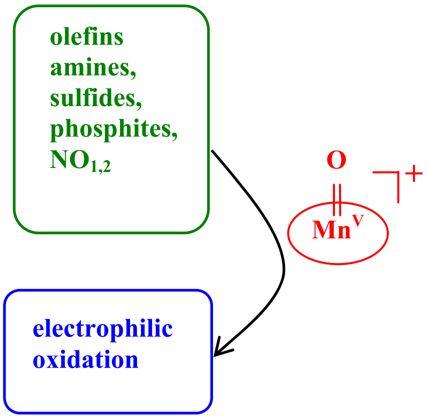
Among biomimetic oxidants developed to disclose the mechanistic routes operative in several metal catalyzed biological and industrial processes, high-valent transition metal-oxo species have been investigated for their function as putative intermediates in mono-oxygenases biochemistry. Although endowed with high reactivity and versatility in various oxidation reactions, manganese(V)–oxo species have eluded detection until recently [1].

Because the nature of these catalysts are strongly affected by several factors, including the pH, the presence and the nature of a trans axial ligand, and the electron promotion energy of the oxidant, gas phase studies may represent a powerful tool to elucidate the complex role of environmental factors as distinct from the intrinsic features of these active species.

We have succeeded in accessing a genuine ligand-free Mn^{V}-oxo porphyrin ion, [(TPFPP)Mn^{V}O]$^{+}$ (TPFPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphinato dianion), **1**, prepared in methanol solution by controlled treatment of (TPFPP)Mn^{III}Cl with iodosylbenzene, gently transferred in the gas phase by electrospray ionization (ESI) and characterized by assay with Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The oxidation ability of **1** towards a range of different substrates, including olefins [2], amines, sulfides, phosphites and nitrogen oxides, has been obtained by the direct determination of reaction patterns and thermal rate constants.

The reaction pathways are initiated by electron transfer and yield products reflecting delivery of oxygen and hydrogen atom, besides hydride and electron transfer processes. Valuable insight into fundamental properties such as the basicity and electron affinity of the ferryl,(TPFPP)Fe^{IV}O, versus the manganyl, (TPFPP)Mn^{IV}O, unit have been also gathered, which can help to elucidate and generalize reaction mechanisms in bioinorganic oxidations.



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INO-PO-68 Interactions of Cisplatin with Adenine and Guanine Nucleobases: a Spectroscopic-Mass Spectrometric study

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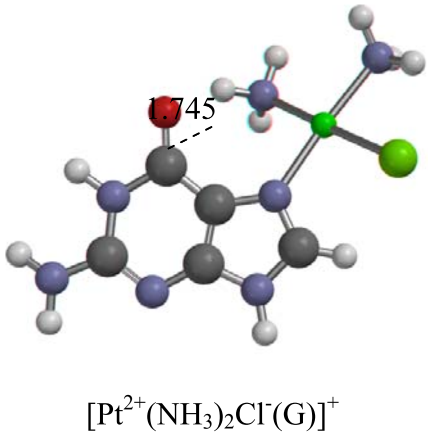
It is the aim of the present contribution to provide an accurate characterization of $[\text{cis-Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{G})]^+$ and $[\text{cis-}[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{A})]^+$, model of the monofunctional adduct between cisplatin and the nucleobases of DNA, using IR spectroscopy of ions directly performed in the cell of a mass spectrometrer. Whereas conventional absorption spectroscopy of gaseous ions is not feasible due to the typically low number density of the sample species, the IR features of a gaseous ion may be disclosed in the IR Multiphoton Dissociation (IRMPD) spectrum reporting the resonance enhanced photofragmentation process following multiple photon absorption in correspondence with the IR active modes of the sampled species. To this end a spectroscopic methodology is applied, based on the coupling of the radiation output of an IR free electron laser (FEL) at the CLIO (Centre Laser Infrarouge d'Orsay) European facility with a Paul-type ion trap mass spectrometer, exploiting the potential emerging from the combination of mass spectrometry with an IR FEL radiation source. The ions of interest have been formed in solution, transferred in gas phase by an ESI source, stored in an ion trap and submitted to IRMPD spectroscopy.

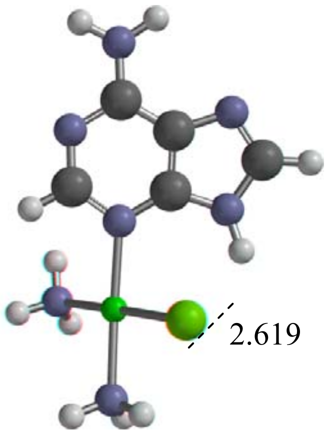
Quantum chemical calculations at B3LYP/6-311G(d,p) level of theory, using the LANL2DZ pseudo-potential basis set for Pt, yield the optimized geometries and IR spectra for the conceivable isomers of $\text{cis-}[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{G})]^+$ and $\text{cis-}[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{A})]^+$, whereby the cisplatin residue is attached to the N7, N1 and N3 positions of the guanine or adenine base.

Both the computational results and the IR characterization point to a covalent structure for the $\text{cis-}[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{G})]^+$ where Pt is bound to the N7 atom of guanine while in the $\text{cis-}[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{A})]^+$ complex Pt is bound to the N3 position of adenine.

To complete the study, measurements of CID (collision induced dissociation) breakdown curves for the selected ions have allowed to determine the apparent binding energy of the Pt complex with the nucleobases showing that the binding energy between Pt and G is greater than that between Pt and A.



$[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{G})]^+$



$[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}^-(\text{A})]^+$

INO-PO-69 New High-Nuclearity Ni-Pd Carbonyl Clusters: $[HNi_{30}Pd_5(CO)_{41}]^{5-}$ and $[Ni_{66}Pd_{10}(CO)_{69}]^{6-}$

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A re-investigation of the reaction of $[Ni_6(CO)_{12}]^{2-}$ with $[Pd(MeCN)_4]^{2+}$ in THF affords the new $[H_{6-n}Ni_{30}Pd_5(CO)_{41}]^{n-}$ (n=2-4) and $[Ni_{66}Pd_{10}(CO)_{69}]^{6-}$ clusters, whose metal frames are reported in Figures 1 and 2. The latter represents the highest-nuclearity homoleptic metal carbonyl anion so far reported and structurally characterized. The metal frame of the $[HNi_{30}Pd_5(CO)_{41}]^{5-}$ cluster is identical to that of the previously reported $[Cu_{5-x}Ni_{30+x}(CO)_{40}]^{5-}$ (x = 0,2) [1].

Previously known examples of Ni-Pd homoleptic carbonyl anions were species such as $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$, $[Ni_{26}Pd_{20}(CO)_{54}]^{6-}$ [2] and $[Ni_{36}Pd_8(CO)_{48}]$6- [3] which were obtained by reaction of $[Ni_6(CO)_{12}]^{2-}$ and $PdCl_2$ or $[PdCl_4]^{2-}$.

The reaction pathway that occurs in solution between Ni and Pd is proved to be rather complex: by changing even one of the boundary conditions (reagents, solvent, reactant molar ratios, temperature, reaction time) the nature of the products may be profoundly influenced.

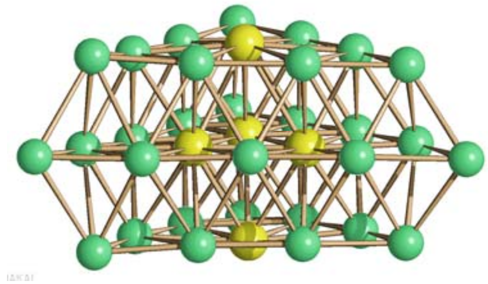

Figure 1
Metal frame of the $[HNi_{30}Pd_5(CO)_{41}]^{5-}$

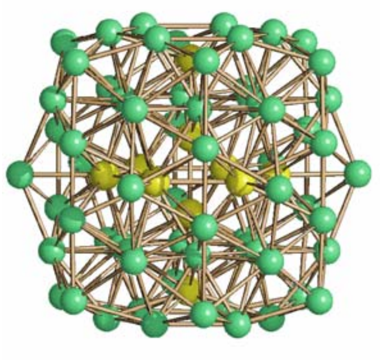

Figure 2
Metal frame of the $[Ni_{66}Pd_{10}(CO)_{69}]^{6-}$

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INO-PO-70 Vibrational behavior , microstructure and morphology of Zinc Ferrite obtained with differing fuels

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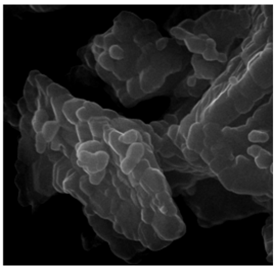
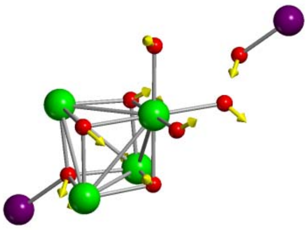
Zinc Ferrite (ZF) is an important oxidic material due to its versatile magnetic and electric properties, that finds wide applications in the field of gas sensors, contrast agents, magnetic materials, photocatalist, etc. A synthetic procedure which permits a fine control of purity and crystallinity of nanoparticles is sol-gel autocombustion method. Many fuels have been explored and their influence on the structure and properties of the spinel-type material has been studied.
In this communication we report the vibrational results of ZF samples obtained by sol-gel autocombustion method using the following fuel agents: citric acid, tartaric acid, urea, glycine, white egg, glucose. Infrared (in the MIR and FIR region) and Raman spectra of samples have been recorded and a complete assignment has been proposed, with particular attention to the spectral behaviour of the simultaneous presence of normal and inverse spinel structures. A fine evaluation of the effect of differing occupation of the A and B sites of the spinel towards vibrational pattern has been explored by means of a computational modelling in the crystalline state and with a normal coordinate analysis of the crystal structure. A microstructure and morphology comparative study was performed by means of SEM analysis.



SEM picture of ZF obtained with citric acid



A vibrational mode of octahedral B site of ZF

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INO-PO-71 A Report on the Potentialities of Tetrakis(thiadiazole)porphyrazines as Photosensitizers: Singlet Oxygen Production and Liposomal Incorporation

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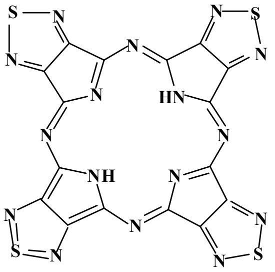
The work on the series of tetrakis(thiadiazole)porphyrazines of general formula [TTDPzM] with M = $2H^{I}$ (see Figure), $Mg^{II}(H_2O)$, Zn^{II}, Cu^{II}, Cd^{II}, $Al^{III}X$, $Ga^{III}X$ and X = OH, Cl, prepared and deeply studied by our group in terms of molecular and electronic structure and physicochemical behaviour, was fairly recently summarized [1]. Moreover, the redox properties of the species [TTDPzM] (M = $2H^{I}$, $Mg^{II}(H_2O)$, Cu^{II}, Zn^{II}) indicated that stepwise reversible or quasi-reversible one-electron reductions lead to the formation of the corresponding $[TTDPzM]^{n-}$ (n = 1÷4) and a detailed DFT/TDDFT theoretical investigation allowed clarification of the electronic structure of all the neutral [2a] and singly one-electron reduced species [2b]. The electrochemical data prove that the all series of compounds behave as highly electron-deficient macrocycles when comparison is made with the behaviour of the related phthalocyanine analogs.



Porphyrins, as well as their azaanalogs phthalocyanines and porphyrazines, are presently intensively investigated as photosensitizers for the generation of singlet oxygen, $^1O_2$, the highly cytotoxic agent in Photodynamic Therapy (PDT). This research field has become in recent years one of the most actively studied by our group [3]. The present contribution will report on the photosensiting properties for the generation of $^1O_2$ of the above series of [TTDPzM] compounds in dimethylformamide solution. Data, showing high photoactivity, will be presented in comparison with similar results for related phthalocyanine and porphyrazine macrocycles. The experimental work, involving partly innovative aspects, has been extended to test the possibility of incorporating the very active Zn^{II} complex into liposome vesicles. The aim is to overcome the insolubility in aqueous media of all these materials with the target of possible clinical applications.

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INO-PO-72 General Properties and Photoactivity of Porphyrazine Macrocycles with Different Degree of π-Electron Delocalization

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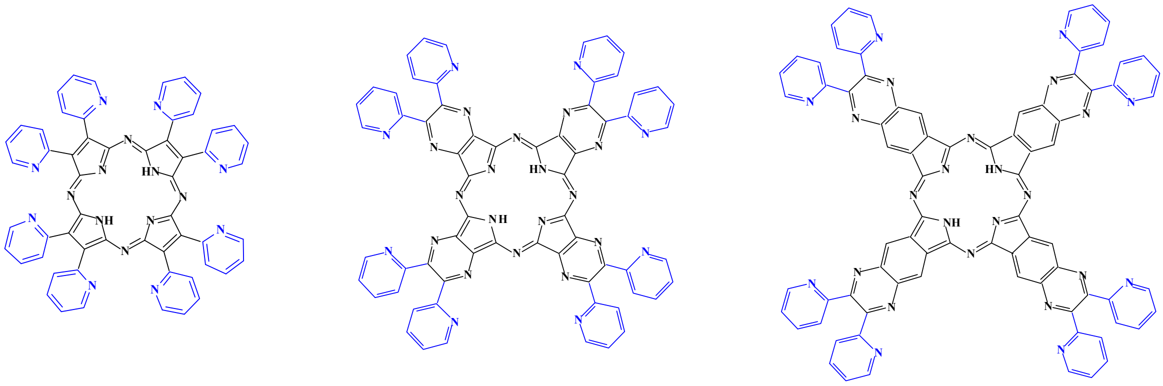
Work in our group was directed to the synthesis and characterization of novel classes of porphyrazine compounds; among them, the pyrazinoporphyrazine macrocycles having formula [$Py_8TPyzPzM$] with M = $2H^I$ (Figure 1B) and bivalent first transition series and non transition series metal ions were deeply investigated. The presence of external electron-withdrawing dipyridinopyrazine fragments strongly influences the electronic structure of the compounds which behave as electron-deficient macrocycles.



A: [Py_8PzH_2] B: [$Py_8TPyzPzH_2$] C: [$Py_8QuinPzH_2$]

Figure 1

A parallel investigation has recently been started on two novel classes of octapyridinated porphyrazines of formulae [Py_8PzM] (Figure 1A: M = $2H^I$) and [$Py_8QuinPzM$] (Figure 1C: M = $2H^I$). The compounds [$Py_8PzMg(H_2O)$] and [$Py_8QuinPzM$] (M = $Mg^{II}(H_2O)$, Zn^{II}, Pd^{II}) have been prepared and their properties studied in the solid state and in solution. UV-visible spectra provide information as to the influence of the different degree of π-electron delocalization in the different types of macrocycles. Two aspects of interest presently under investigation are: a) the ability of the new compounds to act as photosensitizers for the generation of singlet oxygen, $^1O_2$, the cytotoxic agent active in photodynamic therapy (PDT); b) the skill of these macrocycles to generate multimetallic systems by exocyclic metal coordination, already evidenced for the macrocycles of Figure 1B [3, 5].

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INO-PO-73 Coupling of alkynes and bridging ligands in diiron complexes: new route for the formation of functionalized ferrocenes

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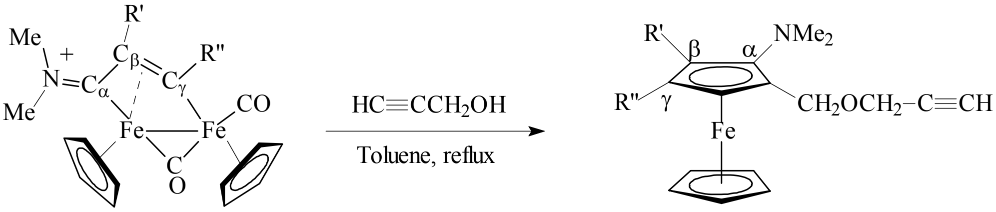
The coupling between small unsaturated molecules and bridging organic ligands in dinuclear complexes provides valuable pathways to the formation of C-C bonds. In particular, the assembling of alkynes with bridging aminocarbyne diiron complexes leads to the formation of μ-vinyliminium ligands, [1] which can be further functionalized, affording variously functionalized C_3 organic frames. [2] Recently we have reported on the possibility of involving the bridging C_3 ligands in cycloaddition reactions with alkynes, with the formation of variously functionalized ferrocenes and cyclohexadienyloxo complexes. [3]
Herein we report on the reactivity of μ-vinyliminium complexes towards propargyl alcohol.



The overall result of the reaction is the one-pot synthesis of a propargyl ether-functionalized ferrocene, in that one molecule of propargyl alcohol is involved in the [3+2] cycloaddition with the C_3 bridging ligand, while another molecule gives rise to the $–OCH_2C≡CH$ group, with loss of one molecule of water.

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INO-PO-74 Metal-Mediated Multi-Chromophore Assemblies: A Structural Overview

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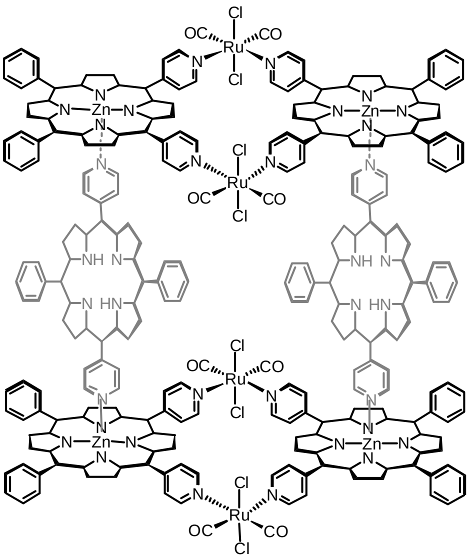
Porphyrins play a major role as active chromophores in artificial systems mimicking the natural photoinduced processes. The formation of coordination bonds between peripheral donor sites on the porphyrins and external metal fragments has proved to be an efficient alternative to covalent synthesis for the construction of multi-porphyrin assemblies, whose complexity and beauty gradually approach those of the multichromophore systems found in Nature.

In a modular approach, relatively simple metal-mediated porphyrin adducts, such as the zinc-porphyrin metallacycle, owing to their thermodynamic and kinetic stability, can be exploited as building blocks in the construction of higher order architectures. We reported that axial ligation of two of these metallacycles by two *trans* bispyridyl porphyrins (4'-*trans*DPyP) led to the formation of molecular box (Figure), both in solution and in the solid state [1, 2].



With the aim to synthesize molecular boxes with different dimensions and photophysical properties, the reactivity of the zinc-porphyrin metallacycle towards a series of other photoactive ditopic nitrogen ligands (such as perylenes) was investigated both in solution and in the solid state [1-3]. The photophysical properties of these novel assemblies have also been investigated [3, 4], but will not be discussed here. Examples in which the X-ray structural determination was essential to establish the real composition and geometry of these multi-chromophore assemblies are highlighted.

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INO-PO-75 Band Gap Engineering in TiO_2 by bulk and surface doping with p-block elements. A reliable perspective for visible light absorption.

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One of the limits for the applications of TiO_2 in photocatalytic systems for abatment of pollutants or in performing up-hill reactions such as hydrogen production by water photosplitting, is the wide band gap (3.2 eV) of this semiconducting oxide which imply the use of UV photons for the promotion of valence band electrons in the conduction band. The modification of the electronic structure of the solid in order to allow the use of visible light in its applications has therefore a paramount importance and two generations of chemically modified titanium dioxide nanomaterials are now available The first generation is that of TiO_2 containing transition metal ions and the second one is that based on doping by non metallic elements. The elements mainly employed in the doping are N, C, S, B and F. An intense debate has grown in the literature, aiming to identify the nature of the doping centers and the reason of the photoactivity in the visible of the doped solids. Some elements of confusion, however, are still present often caused by interpretations based on unreliable hypotheses or on weak experimental grounds.

Our group has attempted, since 2005, to contribute in understanding the role of non metal centres in TiO_2 bulk and at its surface. We have been focused, in particular, on those centers playing some role in visible light absorption[1-4]. This has been done trying to identify well defined centers and to distinguish them from byproducts of preparation reactions having often no role in interaction with light photons.

In this contribution the features of systems based on N doped, F doped, N-F and N-B co-doped TiO_2, prepared in our lab, will be discussed in the aim of elucidating the nature of the photoactive species, the chemical pathway for their formation and the electronic structure of the doped materials. Various experimental tools were employed for this purpose and the most persuasive results were obtained by coupling EPR spectroscopy with state-of-the-art theoretical calculations performed by the group of G. Pacchioni (University of Milano Bicocca).

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INO-PO-76 Catalysis by Group IV Amido-Pyridinate Complexes for the Efficient and Selective Olefin Upgrading; Beware of Metal Precursors!

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Much current interest in organometallic chemistry is linked to the academic and industrial quest for novel types of efficient and selective olefin oligomerization and polymerization catalysts. An improvement of their catalytic performance implies a precise control of the metal coordination sphere, commonly accomplished by a fine tuning of the steric and electronic properties of the ancillary ligands. Nitrogen donor ligands (imines, amides) have proven to be versatile components of bi- and polydentate ligands for the preparation of transition[1] and rare-earth[2] metal complexes in polymerization catalysis.

A recent work by our group on amino-pyridinate ligands in combination with Group IV transition metal precursors [$M^{IV}(NMe_2)_4$ and/or $M^{IV}(Bn)_4$; M = Zr, Hf] has shown a non-innocent role of the precursor species ultimately unveiling unexpected reactivity paths.[3]

Selected Zr^{IV}-amidopyridinate complexes from the same series have revealed outstanding polymerization activities in the production of poly(1-henene). An in-depth study on the nature of the catalytically active species, in combination with the characteristics of the polymers produced (molecular weights, tacticity and regioerror distribution in the polymer microstructure) have demonstrated a close dependence of the nature of the active species from the catalyst aging-time.[4] In the light of the well established efficiency of the Zr^{IV} and Hf^{IV} complexes for the production of specialty polyolefins[5], the result presented in this study provide a useful reference to gain further insight into the wealth chemistry of the nitrogen based early transition metal complexes.

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INO-PO-77 Novel Coinage Metal-NHCs Complexes Derived from Triazoles, Imidazoles and Related Chelating Systems.

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Coinage metal-NHCs are widely studied for their intriguing structural properties and numerous applications [1]. Ag(I)-NHCs are the most studied among coinage metal-NHCs due to their easy preparation via the Ag_2O route and because they are sources of other metal-NHCs through transmetallation. In addition, their different properties in bonding, structure and potential applications in medicine, nanomaterials, liquid crystals, and organic catalysis also contribute to the attraction of Ag(I)-NHCs. Recently we have explored the synthesis of pincer scorpionate type carbene ligands such as the bis(4-benzyl-1,2,4-triazol-4-ium-1-yl)dihydroborate, $\{[H_2B(BnTzH)_2]Br\}$, and related carbene-silver(I) and gold(I) complexes $\{Ag_2[H_2B(BnTz)_2]_2\}$ and $\{Au_2[H_2B(BnTz)_2]_2\}$ [2]. We have also studied trimetallic carbene complexes of general formula $\{Ag_3[HB(RIm)_3]_2\}Br$ (R = Bn, Mes and ^{t}Bu), which were successfully employed in the synthesis of related gold(I) complexes by transmetallation; the silver complexes also proved to be active catalysts in the Sonogashira reaction [3]. Analogous trinuclear copper(I) complexes with triscarbene ligands have been synthesized and proved to be efficient catalysts of Ullmann-type reactions as well as of the Sonogashira reaction. Moreover we have also reported the synthesis of hydrophilic bimetallic complexes of general formula $\{Na_2[H_2C(Tz^R)_2]_2Ag_2\}$ and $\{Na_2[H_2C(Im^R)_2]_2Ag_2\}$ (R = $PrSO_3$ or EtCOO) [4] by treatment, in degassed water solution, of the triazolium or imidazolium species with Ag_2O. As an extension of this research field, we have developed the chemistry of some new water soluble zwitterionic mono-NHC ligands, where imidazolium rings have two alkylsulfonate or alkylcarboxylate side arms. Here we present the synthesis and characterization of these novel hydrophilic carbene ligand precursors $\{HIm^{1R,3R}\}$ (R = $PrSO_3$ or CH_2COOEt) and the related silver(I) carbene complexes of general formula $\{(Im^{1R,3R})AgCl\}$. Gold(I) and copper(I) complexes have been prepared by transmetallation reactions.

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INO-PO-78 Ruthenium(II/III) Complexes of S-donor Ligands: Synthesis, Characterisation and *in vitro* Cytotoxic Activity toward Non-Small Cell Lung Cancer.

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In recent years ruthenium complexes have attracted much attention as promising antitumor and antimetastatic agents with potential uses as an alternative to cisplatin. To date, two ruthenium-based drugs, NAMI-A and KP1019, have reached human clinical testing. These complexes show low systemic toxicity, non cross-resistance and a different mechanism of action compared to platinum containing compounds.[1,2]

During the last decade, our research group has been designing a number of metal–dithiocarbamato complexes (*e.g.* Pt(II), Pd(II), Au(I), Au(III), Ru(III), Zn(II), Cu(II)) that have been tested, at least preliminarily, for their *in vitro* cytotoxic activity toward a panel of human tumor cell lines.[3] Among all, gold(III) complexes have shown outstanding *in vitro* and *in vivo* antitumour properties and reduced or no systemic and renal toxicity, compared to the reference drug.[4,5]

Here we present the syntheses of different Ru(II) and Ru(III) dithiocarbamato complexes: the diamagnetic neutral monomer $[Ru^{II}L_2(dmso)_2]$, the paramagnetic neutral $[Ru^{III}L_3]$ monomer, the antiferromagnetically coupled ionic α-$[Ru^{III}{}_2L_5]Cl$ and β-$[Ru^{III}{}_2L_5]Cl$ dinuclear species, where L = dimethyl- (DMDT) and pyrrolidine- (PDT) dithiocarbamate. All the obtained complexes were fully characterized by elemental analyses, NMR, FT-IR and UV-visible spectroscopies, and in some cases by X-ray analysis. The preliminary *in vitro* cytotoxicity assays on human tumor cells (H1975 non-small cell lung cancer (NSCLC) line) have shown significant antitumor activity of both the monomer and dinuclear Ru(III) complexes.

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INO-PO-79 Palladium nanoparticles synthesized by lignin: an efficient catalyst for C-C cross-coupling reactions

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Metal nanoparticles in water represent useful catalysts because they can operate in environmentally benign conditions. Also their catalytic efficiency is often higher since their high surface to volume ratio [1].

In the present contribution we report both the green synthesis of Pd nanoparticles using a renewable and abundant feedstock like lignin and their use as catalysts in C – C cross coupling reactions (Suzuki [2], Heck [3], Stille [4], Negishi [5]).

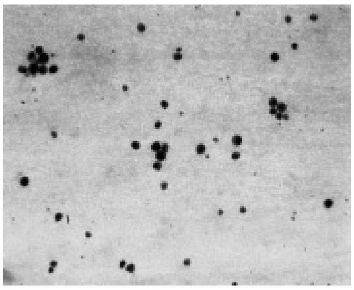

Figure 1: TEM immage of lignin stabilised Pd nanoparticles

G-Ph-I + **Ph-B(OH)$_2$** $\longrightarrow$ **G-Ph-Ph**

Substrate	% Product yields
G = -H	80
G = -OH	100
G = -NH$_2$	80
G = -COOH	70

Experimental conditions: 0.5 mmol of aryl halide, 0.75 mmol of boronic acid, 1.75 mol of base (K_2CO_3), 5 mL of H_2O, 0.2 mL of nanoparticles solution (5.6 mM is the initial conc. of Pd^{II}), 12 hours of react. time and 80 °C of temp.

Two commercial lignins are able to reduce Pd^{II} in water solution forming stabilised Pd nanoparticles of about 19 nm (by TEM analysis) with a a face-centred cubic metal crystal structure (by XRD analysis). We show the results of Suzuki coupling while we will report in the communication of the congress the results about the Heck, Negishi and Stille reactions, all carried out in water under mild condition. No care to exclude air was necessary.

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