Società
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Divisione di Chimica Inorganica

XLIX CONGRESSO NAZIONALE DI CHIMICA INORGANICA

PERUGIA 12-15 SETTEMBRE

INORG2023

BOOK of ABSTRACTS

http://inorg2023.chm.unipg.it

Welcome!

It is a great honour and pleasure for us to welcome you in Perugia at the XLIX Italian Conference of Inorganic Chemistry (September 12-15, 2023).

The congress will showcase Plenary and Keynote lectures from renowned international scientists, as well as oral presentations and poster sessions, spanning topics ranging from compounds to extended materials, with a particular focus on how advances in Inorganic Chemistry, from synthesis to characterization to computation, provide a key launch platform for innovations in real world applications. Subtopics will include coordination & supramolecular chemistry, organometallic chemistry & catalysis, magnetochemistry, energy & photochemistry, green & bioinorganic chemistry, inorganic materials & nanoparticles, medicinal chemistry, and theoretical inorganic chemistry.

Sharing ideas across the very broad spectrum of Inorganic Chemistry field, hopefully enabling the formation of new collaborations and networking in the emerging areas of research, is the main aim of the conference.

Located in the center of Italy, Perugia and its unique atmosphere will provide inspiration for a fruitful scientific meeting and the participants will have time to enjoy culture and historical places in the city.

We wish you a pleasant and fruitful time in Perugia!

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PLENARY LECTURES

PL1

METAL COMPLEXES FOR MAGNETIC RESONANCE IMAGING

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MRI has reached a primary position among the *in vivo* diagnostic techniques. Its images report about the topological distribution of the water proton signal whose intensity depends, first of all, on the proton relaxation times and on the applied acquisition protocol. It was early recognized that the contrast agents (CA) for this imaging modality could be based on paramagnetic substances able to affect the water proton relaxation times in the region where they distribute. The candidates of choice were identified in the class of Gd(III) complexes[1] and since then a plethora of studies have been reported on the structural and dynamic determinants of the parameters that affect the properties of these complexes as CA for MRI (thermodynamic and kinetic stability, relaxivity, solubility, biocompatibility, etc.). Nowadays about 40% of the MRI scans acquired in the clinical settings make use of Gadolinium bearing contrast agents (GBCA). They add physiological information to the superb anatomical resolution attainable in MR images. The optimization of the GBCAs brought important insights to a better understanding of the properties of metal complexes such as the exchange of the coordinated water, the relaxation mechanisms and the set-up of supramolecular interactions with biological substrates, etc. In the last decade, the observation that tiny amounts of gadolinium can be retained in the brain and other tissues in patients treated with GBCAs[2] has brought an increased attention to the design ofparamagnetic complexes of Fe(III) and Mn(II) as MRI CAs.

Besides the class of contrast agents based on relaxation enhancers, much interest is currently devoted to the class of contrast agents based on the exploitation of the transfer of saturated magnetization from mobile protons that are properly saturated by the application of a rf field at their NMR absorption frequency (CESTagents).Again paramagnetic transition metal and lanthanide ions appear particularly suitable for the design of efficient agents (paraCEST).[3] Thanks to their characteristic of being frequency-encoding systems, more agents can be visualized in the same anatomical region and when more than one source of exchangeable protons are present on the same molecule, they can be exploited as responsive agents whose response does not need the knowledge of their actual concentration.

Finally, it will be shown how the presence of a paramagnetic GBCA in the extracellular space affects the CEST properties of intracellular molecules thus allowing to extract information on the water exchange across the cellular membrane. The assessment of active water cycling is highly relevant to report on tumor cell metabolism.

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PL2

METALLACROWN COMPLEXES: HOST-GUEST INTERACTION PAVING THE WAY FOR SMMs

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Metallacrown Complexes (MCs) are composed of metal ions and bridging ligands that form cyclic ring structures in a self-assembly reaction.[1] These complexes have been extensively studied in the past years for their coordination ability with hydroxamic acid and derivatives, particularly with first-row transition metal ions. The atomic arrangement in MCs allows for adjustable magnetic exchange between the metal ions within the ring structure. By employing the magnetic director approach, high spin ground states in MCs have already been achieved.[2] The most important requirement for switchable SMMs, however, is anisotropy. We therefore aimed to implement transition metal ions able to contribute significantly with high single ion anisotropy. In this presentation, I will discuss our approach, which involves enhancing the overall magnetic anisotropy by incorporating lanthanide ions in 3d-4f-metallacrowns.[3] These systems exhibit SMM behavior and hold promise for future applications in data storage, quantum computers, and molecular electronics, as discussed in physics, chemistry, and materials science.

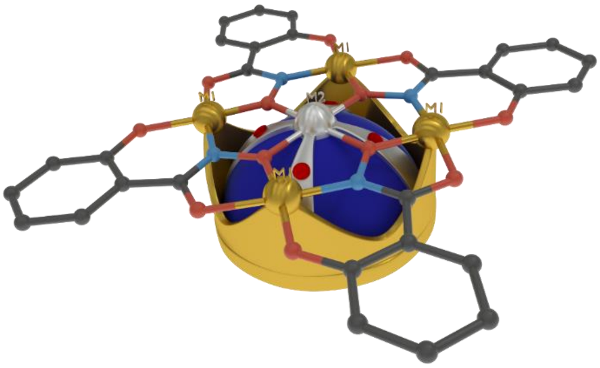

***Figure**: artistic representation of a metallacrown*

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PL3

ZIEGLER-NATTA CATALYSTS AND POLYPROPYLENE: A CONTROVERSIAL STORY

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When the 1963 Nobel Prize in Chemistry was awarded jointly to Karl Ziegler and Giulio Natta, no one anticipated the fierce anti-plastics sentiment of society in the new millennium. To a hypocritical majority, being a Ziegler-Natta chemist in 2023 looks like a perversion, that can only be confessed to the few other degenerates cultivating the same shameful passion in dark corners. This lecture is an opportunity for my coming out. I will tell the story of a class of heterogeneous catalysts that a 1979 book by John Boor[1] rightfully defined as "unique and marvelous". Unfortunately, Boor's premature death prevented him from witnessing how, from the first simple $TiCl_3$-based systems that he contributed to formulate, new generations of sophisticated inorganic-organic catalysts were engineered with unbeatable values of turnover number, frequency and enantiomeric excess.[2] On top of that, I will make the point that converting fossil C into polyethylenes and polypropylenes is mandatory for mankind to survive.

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PL4

TAMING METAL(LOID) COMPLEXES AND THEIR EXCITED STATES FOR OPTOELECTRONICS

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Luminescent compounds are attracting a great deal of attention also due to their appealing application in real-market technologies, such as electroactive materials in light-emitting devices (e.g. organic light-emitting diodes - OLEDs) as well as photoactive bio-imaging and theragnostic agents, amongst others. In this framework, achieving bright emission in the red and near infrared (NIR) region is intrinsically highly challenging and efficient red/NIR light-emitting devices are still scarce to date, despite their importance in fields such as displays, biomedical devices for phototherapy and telecommunication technology.[1] In the first part of the talk, our most recent results in the field will be presented that are mainly based on dinuclearization strategies to finely modulate both ground and excited states in phosphorescent transition metal complexes. [2] On one hand, selective management of the excited- state mixing between singlet and triplet manifolds enabled the preparation of highly emissive red heterobimetallic IrIII/MI complexes. Their successful application as electroluminescent materials in solution-processed light-emitting electrochemical cells (LECs) allowed to achieve external quantum efficiency up to 6%: one of the highest to date for red LECs.[3-4] On the other hand, Cu(I) complexes are an attractive alternative to those based on rarer and more expensive platinum-group metals. To date, Cu(I)-based emitters typically display luminescence from blue to orange, while achieving deep-red to near-infrared (NIR) emission is still very difficult. In this framework, we will present a series of novel bimetallic Cu(I) complexes that display NIR luminescence with maximum emission, lem, max up to 790 nm. In the X-ray structure, the compounds show a doubly locked architecture involving two p-p stacking interactions that helps to mitigate excited-state quenching processes and structural flattening that typically occur in Cu(I) emitters. For the first time, stable Cu(I)-based NIR electroluminescence (EL) is demonstrated with lEL, max up to 756 nm in LECs. [5] Finally, we will turn our attention towards the use of abundant metalloids complexes, such as Si(IV), and a family of highly emissive and stable hexacoordinate Si(IV) N-heterocyclic carbene complexes will be presented that display efficient deep-blue emission.[6]

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PL5

MOLECULAR PHOTOVOLTAICS AND THE RISE OF PEROVSKITE SOLAR CELLS

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Photovoltaic cells using molecular dyes, semiconductor quantum dots or perovskite pigments as light harvesters have emerged as credible contenders to conventional devices. Dye sensitized solar cells (DSCs) use a three-dimensional nanostructured junction for photovoltaic electricity production and reach currently a power conversion efficiency (PCE) of over 15 % in full sunlight. They possess unique practical advantages in particular highly effective electricity production from ambient light, ease of manufacturing, flexibility and transparency, bifacial light harvesting, and aesthetic appeal, which have fostered large scale industrial production and commercial applications. They served as a launch pad for perovskite solar cells (PSCs) which are presently being intensively investigated as one of the most promising future PV technologies, the PCE of solution processed laboratory cells having currently reached 26.1%. Present research focusses on their scale up to as well as ascertaining their long-term operational stability. My lecture will cover our most recent findings in these revolutionary photovoltaic domains.

PL6

ALTERNATIVE ENERGY DRIVERS IN PALLADIUM CATALYZED COUPLING REACTIONS

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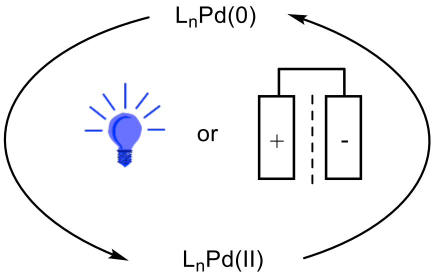
The ability of transition metal catalysts to mediate new bond forming reactions has had a dramatic impact on modern molecular synthesis. Nevertheless, a central feature in these reactions is need to balance of reverse operations on the catalyst so it is regenerated at the end of each cycle of product formation, which can limit catalytic activity and the scope of many transformations. This talk will describe our efforts to address these challenges by introducing alternative, often renewable, energy sources into catalysis, and from this create new bond forming reactions. These include using visible light excitation directly on active palladium catalysts to drive the oxidative addition/reductive elimination cycle in coupling reactions independent of the classical limits in thermal catalysis, or the use of electrochemistry to change the nature of the metal throughout the cycle.[1] Combining these with the favored energetics of carbon monoxide conversion to carboxylic acid derivatives can be used to drive the build-up of reactive products from stable reagents. The use of this chemistry to create ambient temperature and general catalysts for carbonylation reactions, multicomponent transformations, acyl halide or even super-electrophile formation, or new avenues to C-H bond functionalization, will be discussed, as will the mechanistic origins of these influences, and their ability to enable the use of earth abundant catalysts in traditionally precious metal catalyzed reactions.



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PL7

ORGANOMETALLIC CATALYSIS IN CELLS: FROM MECHANISMS TO BIO-APPLICATIONS

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The ability to perform 'new-to-nature' chemical reactions within living cells is transforming the way in which scientists interrogate and manipulate biological processes. In recent years, the toolbox of bioorthogonal chemistry has been enriched with the incorporation of transition metal-mediated reactions. In addition to redox processes, the chemistry of transition metal complexes has been rapidly expanding to other types of transformations in cellular environment, including cross-coupling reactions, cycloadditions, transfer hydrogenation (TH) reactions, as well as functional group deprotection (uncaging) reactions.

This lecture summarizes recent developments for different families of catalytically active organometallic gold compounds including cyclometallatedAu(III) and Au(I) N-heterocyclic carbene (NHC) complexes, and provides insights into their reactivity in biological environments. For example, recent findings from our group on Au(III)-catalyzed reductive elimination in aqueous media constitute the proof-of-concept for the use of cyclometalated Au(III) C^N complexes to achieve efficient modification of proteins through C-atom transfer, enabling chemoproteomic studies (e.g. profiling of cysteine residues) and novel therapeutic approaches.[1] The obtained mechanistic insights have allowed to extend the cross-coupling concept to other substrates, to afford C–P and C–C bond formation under mild conditions,[2,3] relevant to applications of gold compounds in catalysis.

Furthermore, recent results from our group on transfer hydrogenation reactions in cancer cells conducted by water-soluble Ru(II) monocarbonyl complexes with bidentate phosphine and nitrogen-donor ligands - $[Ru(OAc)CO(P^\wedge P)(N^\wedge N)]^n$ (n = +1, 0; OAc = acetate) - will be highlighted.[4] The compounds have been studied for the catalytic regioselective reduction of NAD^+ to 1,4-NADH in aqueous solution with sodium formate as hydride source, as well as for the reverse oxidation reaction of 1,4-NADH in the presence of O_2. TH could be performed in cells and followed by fluorescence microscopy. Ru(II) hydride complex formation could be detected in cell extracts by NMR spectroscopy.

Overall, these examples evidence the power of organometallic chemistry for the design of highly versatile and water-compatible catalytic metallodrugs, and to achieve metal-promoted synthetic chemistry in living systems.

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PL8

SUPRAMOLECULAR CHEMISTRY IN ACTION: FROM MOLECULAR SWITCHES TO SYNTHETIC NANOSCALE MOTORS

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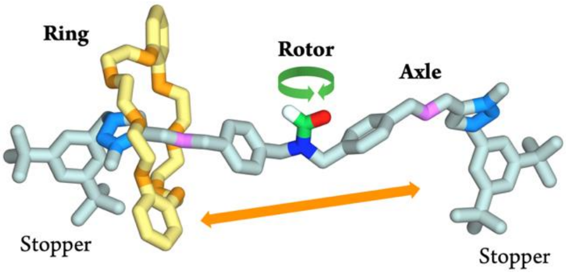
The development of molecular scale devices and machines, enabled by the progress of supramolecular chemistry and related disciplines, has formidably stimulated the creativity of chemists since the 1990s.[1,2] The interest on such systems stems from their ability to perform a (useful) function in response to chemical and/or physical signals (e.g., light). For this purpose, mechanically interlocked molecules exhibit highly appealing structural and functional properties.[1]

Here I will describe a scientific journey, undertaken in the past decade in our laboratories, aimed at understanding how to induce and control dynamic processes in rotaxanes and related species to perform functions[3] such as transmitting information between distant sites, generation of frustrated structures and orientational isomers, switching of mechanically planar chirality, and combining motions of different nature in the same molecule (see figure). From a fundamental viewpoint these systems behave as molecular switches under thermodynamic control. Appropriately designed architectures, however, can exploit an energy harvesting process to operate away from thermodynamic equilibrium. Moreover, by exploiting energy and/or information ratcheting effects, directional and autonomous movement of the molecular components can occur.[1,2] Following this approach, we realized artificial nanoscale pumps powered by light[4] and electricity.[5] Besides the interest for fundamental science, these systems have the potential to bring about radical innovation in catalysis, materials, energy conversion, robotics and medicine.[6]



***Acknowledgements**: Support from the EU (H2020 ERC AdG ‘Leaps’ 692981, FET-OPEN ‘Magnify’ 801378, ITN ‘ArtMoMa’ 860434) and Italian MUR (Grants 20173L7W8K and R16S9XXKX3) is gratefully acknowledged.*

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KEYNOTE LECTURES

KL1

LUMINESCENT NANOCRYSTALS AS LIGHT-HARVESTING ANTENNAE AND PHOTOCATALYSTS

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Within the growing field of luminescent nanocrystals, the present contribution will focus on two families: silicon nanocrystals (SiNCs) and copper indium sulphide (CIS) nanocrystals.
SiNCs in the quantum size range (2-12 nm) display emission wavelength that can be tuned from the near-infrared (NIR) into the visible by decreasing their size.[1]
Silicon nanocrystals, produced by thermal disproportionation of silicon oxide, were co-passivated with dodecene and different organic chromophores, e.g. anthracene.[2, 3] Excitation of the organic chromophores results in an efficient energy transfer to the nanocrystal core: this is the working principle of a light harvesting antenna.
This approach enabled us to circumvent the drawback of the low molar absorption coefficient of SiNCs. The investigated hybrid material exhibits high quantum yield also in the NIR spectral region with lifetime in the µs range. This research has potential applications in imaging, taking advantage of time-gated luminescence microscopy to enhance image resolution and in solar energy conversion, e.g. luminescent solar concentrators, thanks to the apparent large Stokes shift.
CISare ternary semiconducting nanocrystals which displayhighly tunable optical properties.[4] In fact, the synthetic strategy, the Cu-to-In ratio, the dimension of the nanocrystal and the synthesis of a shell are just some of the methods by which CIS-QDs' properties can be adjusted to meet the required properties. The aim of our research is to employ CIS as light-harvesting antennae[5] and as photosensitisers in photoelectrochemical cells. We developed a sustainable approach for the functionalization of FTO-TiO_2 photoanodes with CIS-QDs which allowed high yield, mild conditions and low waste of reagents. The inclusion of CIS-QDs on TiO_2-based photoanodes is convenient because it broadens the absorption properties of the photoanode in the visible spectrum, so to obtain charge separation under solar illumination.

Acknowledgements: *The research has been funded by H2020-RIA project CONDOR and ITN PhotoReact.*

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KL2

SCIENCE AND ART: KNOWLEDGE AND CONSERVATION

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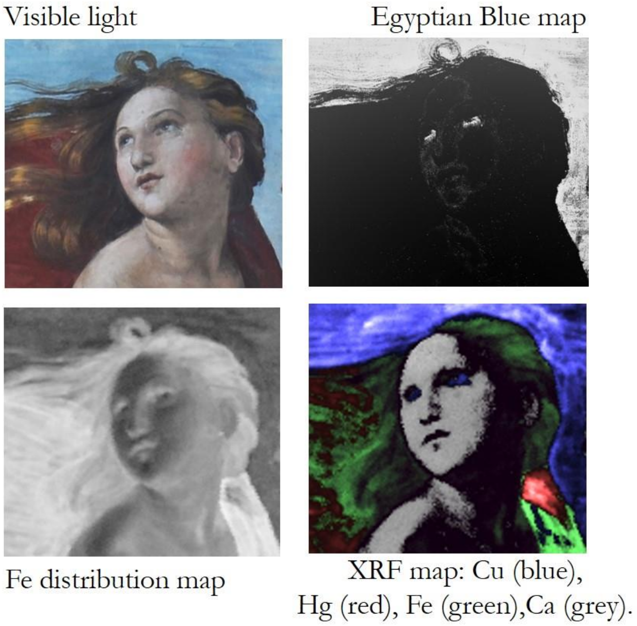
Villa Farnesina, the house of Agostino Chigi designed by Baldassarre Peruzzi, and decorated by the masters of Renaissance painting is one of the highest artistic expressions of this period. The fable of Apuleius, frescoed in the Loggia of Cupid and Psyche byRaphael and hisworkshop, is framed by vegetable festoons: their rich hues associated with fruits from allcontinents represent the colors of prosperity. The chromatic richness of these fruits, many of them still not fully known and never depicted before, is represented by the use of unusual pigments and materials, as revealed by non-invasive investigations. From the study of the materials of the Triumph of Galatea, an autographed fresco by Raphael, the use of Egyptianblue emerged after centuries of oblivion: material evidence – completely unexpected – of thegreat interest of the Urbinate Master for the Antique. Non-invasive diagnostics for cultural heritage is therefore not only a necessary prologue to restoration procedures, but an essential hermeneutic tool for a new history of art, where sometimes the materials themselves tell the artist's intentions like documentary traces. The Villa Farnesina is also the protagonist of a study concerning the impact of fine dust from vehicular traffic on its frescoed loggias and on the garden. The study was conducted through monitoring measures on leaves and lichens, used as bioindicators.



Visible light

Egyptian Blue map

Fe distribution map

XRF map: Cu (blue), Hg (red), Fe (green),Ca (grey).

Raphael, *Triumph of Galatea* (detail).
Villa Farnesina, Rome

KL3

STRUCTURAL DIVERSITY OF LANTHANIDE COMPLEXES. IS IT HELPFUL FOR THEIR SEPARATION AND RECOVERY?

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Rare earth elements (REEs) are widely used in high technologies, and the production of REEs-based permanent magnets (PMs) is one of the fastest growing sectors. The European Commission considers rare earths among the most resource-critical raw materials as they are of the utmost economic importance and present a high supply risk. New rare earth mines are emerging in Europe and urban mines can be exploited for recovery of critical elements.[1]
The combination of Nd and Dy in Nd(Dy)FeB PMs improves their magnetic properties, but makes their recycling more challenging. The separation of Nd and Dy is expensive and the recovery of the two metals from waste materials is currently limited to the small scale. It is therefore of paramount importance to devise efficient and selective methods capable of recovering and reusing those critical elements.[2]While Nd and Dy have very similar chemical characteristics, they have substantial differences (such as ionic radius and coordination number) that allow ligands to be designed that meet the stereoelectronic requirements of either metals. The use of high-denticity ligands (c.n. >7) may result in geometric frustration for one metal rather than another.[3] At the other extreme, mono- or bidentate ligands may generate coordination differences between Nd and Dy. We will show some examples of coordination strategies useful to maximize the difference in solubility between Nd and Dy complexes, aimed at their separation and recovery.[4]

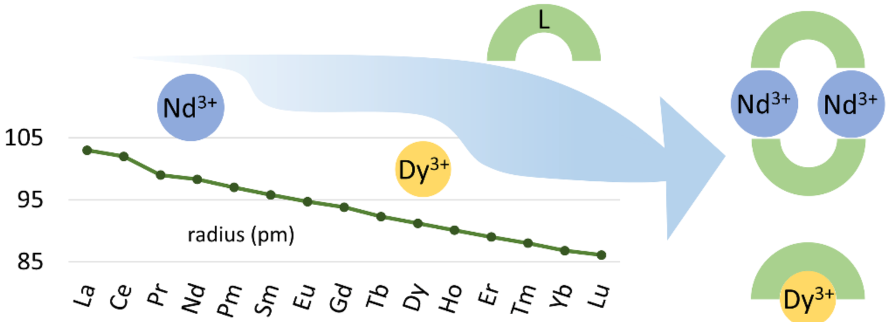

Figure 1

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KL4

CATALYST INNOVATIONS IN POLYETHYLENE

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There has been tremendous progress over the last 30 years in the field of polyethylene (PE). Over this time catalysis has played a central role in expanding what is possible with these materials. While catalysis continues to be paramount in the development of new architectures and functionalities, it is also playing an increasing role in circularity, thus serving as the critical component in both the beginning and end of life of these valuable materials.

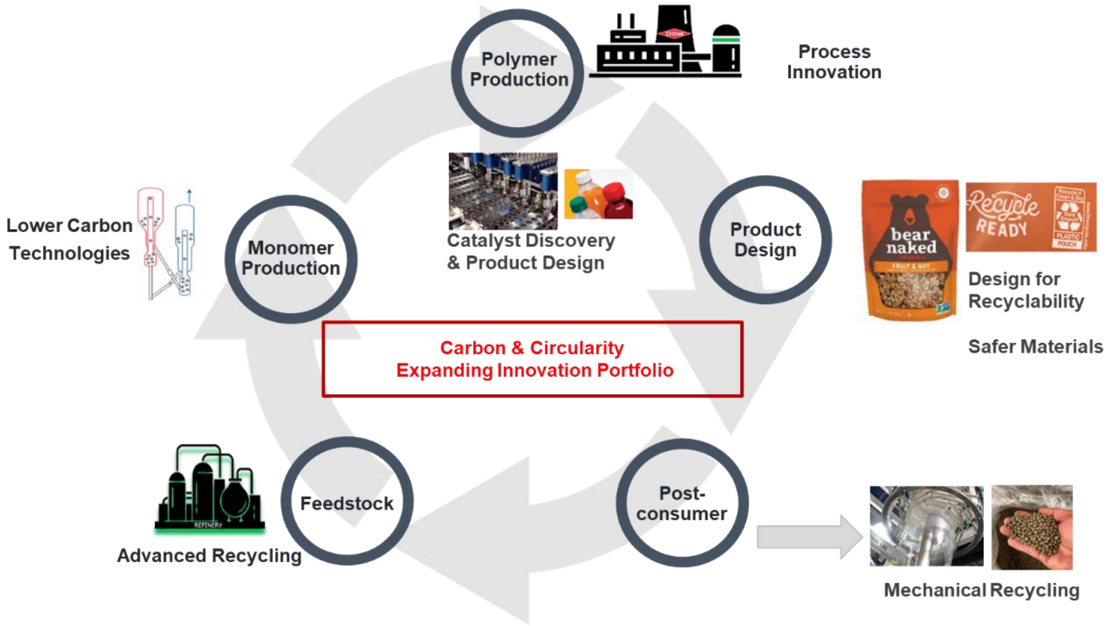

Figure 1*: The polyethylene lifecycle*

This talk will highlight some key innovations being made within the polyethylene lifecycle, focusing on the critical role inorganic and organometallic chemistry are playing in those developments.

KL5

COMPUTATIONAL DESIGN OF MOLECULAR CATALYSTS WITH TAILORED SELECTIVITY

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This contribution highlights ongoing efforts to develop advanced computational techniques to aid the design of molecular catalysts with tailored selectivity.[1,2,3] Our main focus is on understanding the influence of catalyst geometry and electronic structure on the selectivity, which helps to identify design principles for novel synthetic pathways relevant to industry. The application of these techniques is showcased using highly relevant stereoselective reactions as case studies.[3,4,5]

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KL6

IUPAC – BONDING THE GLOBAL CHEMISTRY COMMUNITY

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The International Union of Pure and Applied Chemistry (IUPAC) plays a crucial role in promoting and advancing chemistry worldwide. Through its Committee of Chemistry Education (CCE) is dedicated to improving chemistry education by developing and implementing innovative programs and initiatives that engage and inspire students and educators.[2] One of IUPAC's key activities in the area of chemistry education is the development of educational materials and resources, such as textbooks, laboratory manuals, and online resources. These materials are designed to provide students with a comprehensive and in-depth understanding of chemical concepts and principles. Some examples of this are the IUPAC educational websites[3] its Open Access journal devoted to chemistry education, Chemistry Teacher International,[4] and its International Conferences in Chemistry Education (ICCE).[5] In addition to the development of educational resources, IUPAC also runs several programs aimed at promoting chemistry education.

It is hard to overstate the importance of chemical data and cheminformatics, or the key role that artificial intelligence and machine learning play in chemistry. That is why Digital IUPAC and WorldFAIR have been two of my top priorities during this biennium. IUPAC is actively working through the WorldFAIR initiative to advance the implementation of the FAIR (Findable, Accessible, Interoperable, and Reusable) data principles through the use of chemical data standards in data reporting workflows and tools.

Through the work done by several of its committees, IUPAC also produces materials to teach sustainable chemistry in an effective and engaging way. Currently, we are very active in promoting circular chemistry,[6] systems thinking,[7] and how chemistry can contribute fight against climate change.[8] Furthermore, IUPAC plays a significant role in promoting and supporting diversity and inclusiveness. The organization collaborates with various partners and stakeholders to create initiatives that aim to increase the participation of underrepresented groups in chemistry education, such as women and minorities. An example of this is the Global Women´s Breakfast, a global networking event that every year gathers thousands of people in hundreds of cities around the world to connect, empower, and inspire women scientists worldwide.[9]

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8. Climate Change, The King's Centre for Visualization in Science, https://www.kcvs.ca/details.html?cardName=climateContributions
9. The Global Women´s Breakfast: https://iupac.org/gwb/

KL6

INORGANIC SOLIDS AT THE ORDER-DISORDER BOUNDARY

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Materials at the order-disorder boundary represents a fascinating opportunity to delve into a world of virtually limitless structural possibilities. During the presentation, I will describe the fabrication and application of superior hierarchical catalysts, which lack long-range order but at local scale contain zeolite building units. [1,2] In fact, they are made out of fragments of one or even various zeolite structures and display improved accessibility, strong acidity, and excellent stability. Because of these features, they effectively catalyze reactions involving very bulky molecules, which currently are produced using highly corrosive homogenous catalyst. Using interzeolite conversion, we were able to produce families of materials with controlled amounts of different zeolitic building units and, consequently, optimize their catalytic performance for various reactions including Friedel-Crafts alkylations and Claisen-Schmidt condensations, and the cracking of 1,3,5-triisopropylbenzene. An important advantage of this strategy is that the physicochemical properties and, therefore the catalytic performance, of the hierarchical catalysts can be finely tuned by simply stopping the interzeolite transformation at different times. This creates countless opportunities for the development of hierarchical catalysts [3] with optimized properties and superior catalytic performance for those reactions in which zeolites present significant diffusion limitations (Fig. 1). This paves the way for the fabrication of hybrid hierarchical catalysts with optimized properties for those processes in which the combined use of different zeolites yields improved performance.

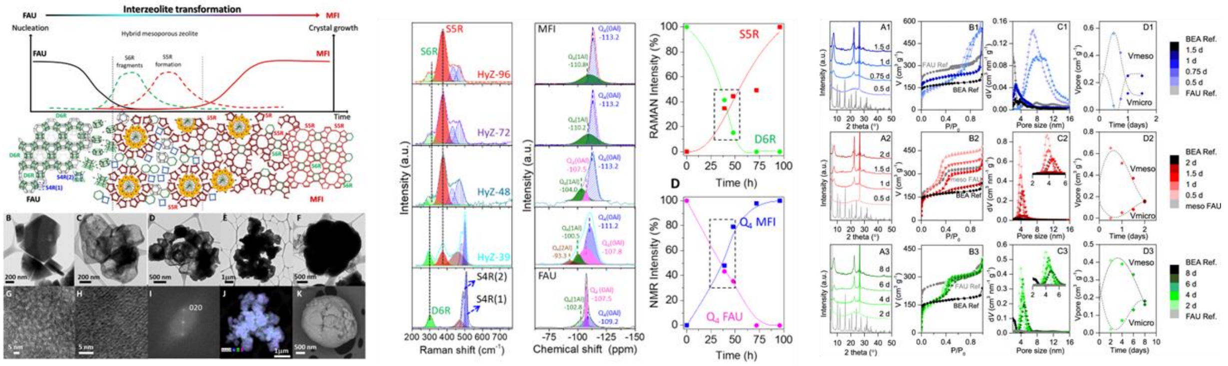

Figure 1. Textural, structural, and morphological characterization of some intermediates of the interconversion of zeolite FAU into MFI and BEA structures.

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KL7

INORGANIC NANOSTRUCTURED MATERIALS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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Nowadays, one of the main technological challenges that we are facing is the ability to provide a sustainable supply of clean energy and, among all renewable sources, solar energy displays the greatest potential.
Recently, the development of novel synthetic strategies has led to the preparation of nanostructured materials displaying unique properties compared to the bulk counterpart systems, with controlled and tunable morphologies able to enhance the activity and selectivity of a heterogenous process.
This talk will focus on the importance of tuning the morphological features of a catalyst as a strategy to improve its photoactivity, focusing on how rationally designing inorganic materials at the nanoscale can lead to shapes and structures suitable to enhance the performance of industrially and environmentally important processes. The talk will discuss some energy and environmental applications that can be addressed by multi-component systems synthesized via the bottom–up approach, highlighting their structure-reactivity relationship. Photocatalytic H_2 production and purification, and drugs degradation will be presented as successful cases history.[1-3]

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KL8

DIFFERENT POLYAZALIGANDS FOR DIFFERENT APPLICATIONS

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The design of receptors able to selectively recognize and bind specific guests is a challenging and dateless target. Polyaza scaffolds are useful tools in this regard, due to their easy functionalization and tunable topology, moreover they provide high solubility in aqueous solution.

Open-chain polyamine ligands ensure flexibility, allowing for the accommodation of metal cations with different sizes and coordination geometries. The presence of multiple aza-binding sites allows for the formation of polynuclear complexes, where the distance between the metal centers can be tuned to have themcooperateor not in the formation of the active site.[1] Moreover, a preorganized polyaza-metal complex canbecome a metallo-receptor for additional guests.[2–4]Macrocyclic polyamine ligands ensure instead high complex stability and selectivity towards the target metal cations, thanks to the preorganization provided by the stiffenedsystem.[5] The insertion in the aza-ligands of suitable further groups, such as chromophores or fluorophores, can help driving the selectivity toward hard or soft species and/or signal the occurred interaction with the guest.[6,7] The additional moiety can be linked to the open-chain or macrocyclic polyamine through a simple spacer or could be part of the macrocycle, forming a cyclophane[8–10](Figure 1).

Our group has always been characterized by the employment of polyaza-scaffolds to build receptors for guests of different nature. In this contribution, some examples of open-chain, macrocycle or cyclophane polyamine ligands are reported, to show their peculiar behavior towardsselected metal ions.

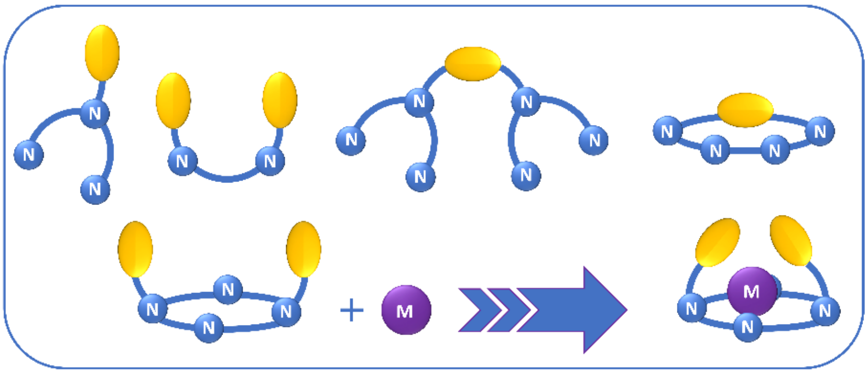

***Figure 1**: Scheme of possible polyaza-ligands and example of metal ion complexation*

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PhD AWARD LECTURES

PhD AWARDS1

DE NOVO DESIGNED COPPER-CONTAINING METALLOENZYMES FOR OXIDATIVE CHEMISTRY

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Copper-containing metalloenzymes are a significant group of proteins found in nature, responsible for catalyzing a wide range of reactions.[1] Among several approaches to studying copper metalloenzymes, de novo protein design represents a valuable strategy to transplant the target copper-binding site in simpler and possibly more stable small-sized scaffolds.[2]

In this work, we showcase the design, characterization, and functional studies of three different de novo designed copper-containing metalloenzymes. Due Rame (DR1) is a de novo designed miniprotein housing the di-copper Type 3 Copper site (Figure 1a) of polyphenol oxidases into a four-helix bundle (Figure 1b). DR1 recapitulates the Type 3 Copper site, supporting several copper redox states and being active in the O_2-dependent oxidation of catechols to *o*-quinones, according to spectroscopic, thermodynamic, and functional analysis.[3] Subsequently, we show that protein design allows the transplantation of the peculiar Type 2 Copper site of Lytic Polysaccharide Monooxygenases (LPMOs), known as Histidine Brace (Figure 1c), into de novo designed scaffolds that differ significantly from the canonical natural fold. To this end we designed dHisB and miniLPMO. These helical bundle miniproteins allowed unraveling for the first time, to the best of our knowledge, the specific contribution to the EPR spectrum of the different protonation states of the Histidine Brace center over a wide range of pH, not always attainable with natural proteins. Noteworthy, these small proteins activate O_2 or H_2O_2 in a similar way to their natural counterparts.

In conclusion, these simple models represent a milestone in the development of synthetic metalloenzymes for the degradation and conversion of biomass into second-generation fuels.

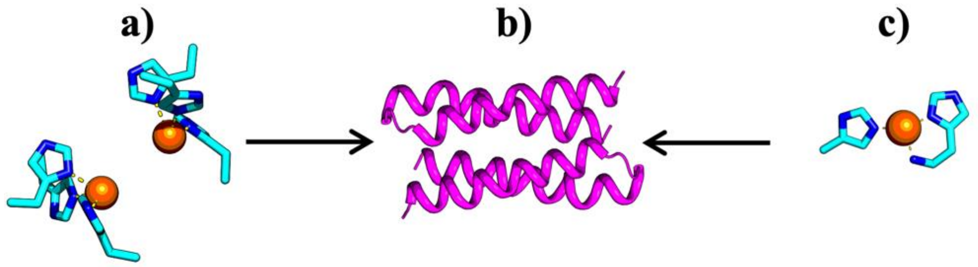

Figure 1: *a) Type 3 Copper site. b) De novo designed scaffold used in this work. c) Type 2 Copper site (Histidine Brace).*

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PhD AWARDS2

ELECTRONIC AND GEOMETRIC STRUCTURE OF COPPER SINGLE-METAL SITES IN ZEOLITES BY HYPERFINE SPECTROSCOPY AND QUANTUM CHEMICAL MODELLING

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Atomically dispersed transition metal ions in zeolites catalyse a wide range of industrial reactions and are at the centre of intense research interest to design new sustainable synthetic pathways forenergy conversion and environment remediation. One of the big challenges in this context is the characterization and location of the active sites. Indeed, mapping their nature with atomic-scale precision occupies a central place in the theory and practice of heterogeneous catalysis.[1]
Here, the site-selectivity and sensitivity of Electron Paramagnetic Resonance (EPR) with its pulsed variants are combined with quantum chemical modelling to determine the microscopic structure of monomeric Cu^{II}species in zeolites with Chabazite (CHA) topology as a function ofthe hydration conditions and sample composition. By isotopic labelling of the zeolite framework with ^{17}O and employing ^{17}O ENDORspectroscopy, the degree of covalency in the Cu-O bond is mapped and the evolution of Cu^{II}sites as a function of the hydration conditions is followed.[2] By combining ^{1}H HYSCORE experiments with state-of-the-art quantum chemical modelling, the EPR signature of the redox active hydroxo-Cu^{II} species is univocally identified and a quantitative assessment of its electronic and geometric structure is provided as a function of zeolite composition.[3]

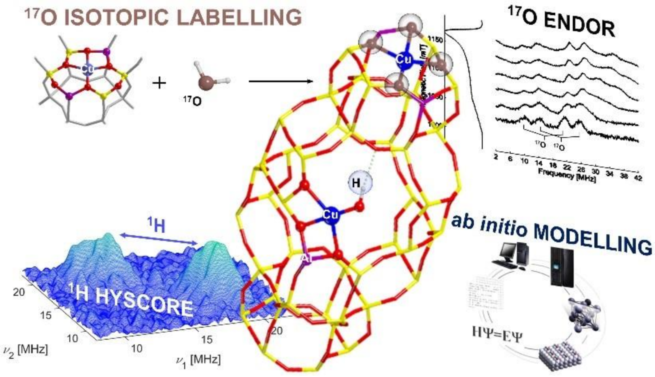

***Figure1**: Pictorial scheme of the approach used in this work.*

***Acknowledgements**: This work is part of a project that has received funding from the European Union's Horizon2020 research and innovation programme under the Marie Skłodowska-Curie Grantagreementno. 813209.*

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PhD AWARDS3

ZINC-BASED CATALYSTS FOR THE SYNTHESIS AND CHEMICAL RECYCLING OF POLYLACTIDE

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Polylactide (PLA) is an aliphatic polyester obtained from renewable sources, it is biocompatible, biodegradable and thanks to its good mechanical properties it can be used to replace common petroleum-based polymers in many sectors. Although these features design a green profile forPLA, its current production and waste management strategies shows some weaknesses in terms of sustainability: PLA is obtained industrially by Ring-Opening Polymerization (ROP) of lactide (LA) promoted by toxic Sn-based catalysts, and its end-of-life management is still aligned to alinear economic model. To include PLA in a more virtuous circular economy model, chemical recycling is a desirable option, as it allows the reconversion of plastic waste into its originalcomponentsand/orintoothervalue-addedmaterials.[1] Zinc complexes, thanks to their high activity and absence of toxicity, offer new opportunities ascatalysts both for synthesis and chemical recycling of PLA.[2] In this context, we introduced a new family of ligands based on a phenoxy-imino framework bearing an additional pyridine moietythat, acting as an hemilable donor, can stabilize the metal center and/or play an auxiliary roleduringthecatalyticreactions.

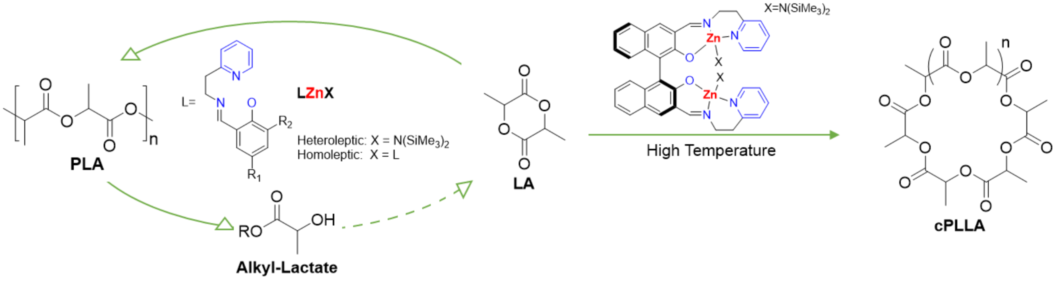

Figure1*: Zn complexes supported by pyridine phenoxy-iminobased-ligand.*

Zinc complexes with different coordination geometries (tetrahedral heterolectic and octahedral homoleptic complexes) and nuclearity (mono-andbi-metallic complexes) have been synthetized and explored as catalysts for the synthesis of PLA. The family of heteroleptic monometallic complexes showed the highest activities classifying among the most efficient catalysts reported in the literature.[3] Surprisingly, the corresponding bimetallic zinc complex showed a marked selectivity towards the formation of cyclic PLA oligomers under specific reaction conditions.[4] Finally, the same complexes were successfully used for the degradation, via alcoholysis, ofpost-consumerPLA. Different mechanisms have been highlighted depending on the conditions adopted (in solution or solvent-freeconditions).[5]

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EURJIC LECTURE

EURJIC LECTURE1

MECHANOCHEMICAL PROCEDURES FOR THE PREPARATION OF RUTHENIUM COMPLEXES

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Mechanochemistry is commonly associated to green chemistry for its ability to reduce waste production in chemical synthesis and reactions. In addition to their efficiency and practicality, mechanochemical reactions are also recognized for their sustainability, especially due to the solvent-free nature of most mechanochemical protocols and due to easy work-up of the reactions. Several works demonstrate the potential of mechanochemistry as an alternative route for fine chemicals production.[1] Ruthenium complexes have been widely investigated and applied in homogeneous catalytic reactions and several Ru-catalysts has been developed, and among all, ground-breaking results have been obtained by Grubbs[2] for the olefin metathesis and Noyori for the asymmetric hydrogenation of the C═O bonds[3].
Here, we investigated the possibility of new synthesis route by mechanochemical methods that can be applied for the preparation of Ru-based complexes precursors or catalysts. As reported in Figure 1, we started with commonly Ru-precursors, like $RuCl_2(PPh_3)_3$), $[(cymene)RuCl_2]_2$, $[(COD)RuCl_2]_2$ $[(CO)RuCl_2]_2$etc., and ligand such as alkali metal carboxylate, diphosphines or N^N ligands to obtain the correspondent Ru-complexes. We studied the role of each reaction variable, such as molar ratio of the reagents, number of balls, frequency and time of milling. Preliminary results suggest that mechanochemical procedures can be a simple and versatile method for the preparation of Ru-based complexes by solventless strategies.

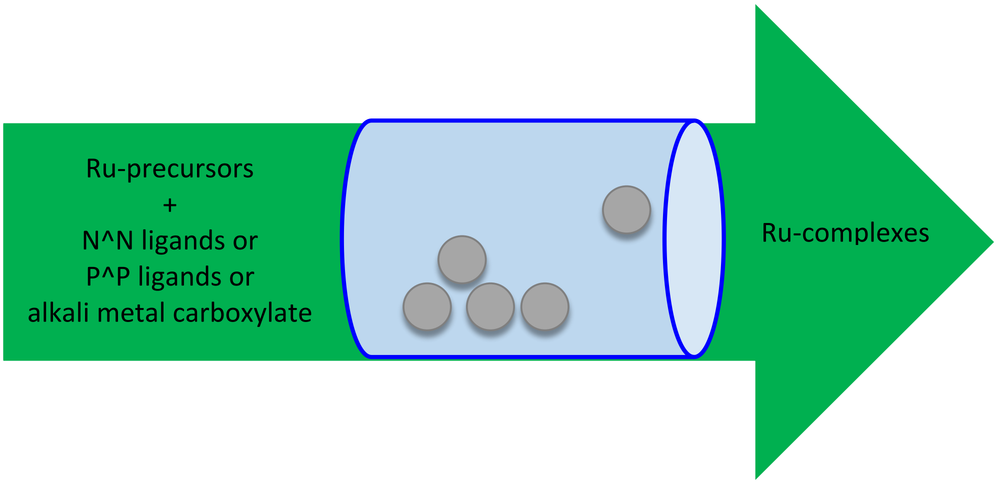

Figure 1*: Scheme of ruthenium complexes synthesis by mechanochemical process.*

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Ad hoc ORAL COMMUNICATIONS

Ad hoc O1A

TAILORED SYNTHESIS OF MIXED-LIGAND MOLECULAR GOLD NANOCLUSTERS

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We report on a new method to synthesize molecular gold nanoclusters (AuNCs) stabilized by a mixed ligand sphere composed of PPh_3 and di-N-heterocyclic carbene (di-NHC) ligands. The method is based on the reaction of a preformed, PPh_3-stabilized AuNC with dinuclear di-NHC gold(I) complexes and enables the production and isolation of clusters with different nuclearity and ligand stoichiometry, depending on the di-NHC properties and reaction conditions.[1] In particular, the interaction of di-NHC gold(I) complexes, with general formula $[(\text{di-NHC})Au_2Cl_2]$ with well-known $[Au_{11}(PPh_3)_8Cl_2]Cl$ clusters provides three new classes of AuNCs through a controllable reaction sequence. The synthesis involves an initial ligand metathesis reaction to produce $[Au_{11}(\text{di-NHC})(PPh_3)_6Cl_2]^+$ (type **1** clusters), followed by a thermally induced rearrangement/metal complex addition with the formation of Au_{13} clusters $[Au_{13}(\text{di-NHC})_2(PPh_3)_4Cl_4]^+$ (type **2** clusters). Finally, an additional metathesis process yields $[Au_{13}(\text{di-NHC})_3(PPh_3)_3Cl_3]^{2+}$ (type **3** clusters). The electronic and steric properties of the employed di-NHC ligand affect the product distribution, leading to the isolation and full characterization of different clusters as the main product. A type **3** cluster (Figure 1) has been also structurally characterized. Type **3** clusters were found to be strongly emissive in solution, reaching quantum yields among the highest ever reported for this kind of molecules.

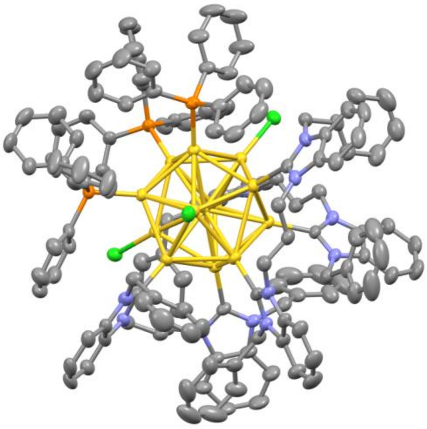

***Figure 1**: Crystal structure of a type 3 cluster $[Au_{13}(\text{di-NHC})_3(PPh_3)_3Cl_3]^{2+}$*

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[1] M. Bevilacqua, M. Roverso, S. Bogialli, C. Graiff, A. Biffis, *Inorg. Chem.* **2023**, *62*, 1383-1393.

Ad hoc O2A

RUTHENIUM BIFUNCTIONAL BASED CATALYTIC SYSTEMS TO TUNE EFFICENCY AND SELECTIVITY IN ALCOHOL HOMOLOGATION

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Bio-ethanol refining is conceived to develop new strategies to second-generation biofuels production. Among others, the Guerbet reaction is an attractive route for the catalytic upgrading of ethanol to linear and branched higher alcohols, which possess greater energy density and miscibility with conventional fuel compared to their lighter analogue. While simple in principle, this is difficult in application due to several concerns encountered in selectivity and conversion. These drawbacks can be partially avoided exploiting homogeneous catalysis.[1]

Here we report on our recent results on the development of new catalytic homogeneous systems for the efficient bio-ethanol homologation under mild conditions. Reactivity is accompanied by DFT calculation in order to understand the mechanism and better drive the design of the process. The synergistic work of a ruthenium cyclopentadienone complex [Ru] for hydrogenation and dehydrogenation, a quite high amount of base that catalyse aldohol condensation and benzoquinone (BQ) as a co-catalyst which favour the selectivity on higher alcohols reducing side reactions, lead to unprecedented catalytic activity (up to 88%) and selectivity (up to 97% in C4-C10 alcohols) under mild conditions (T = 150 °C, t = 4h, [Ru] = 0.2 mol%, BQ = 1.5 mol%, NaOEt = 20 mol%).

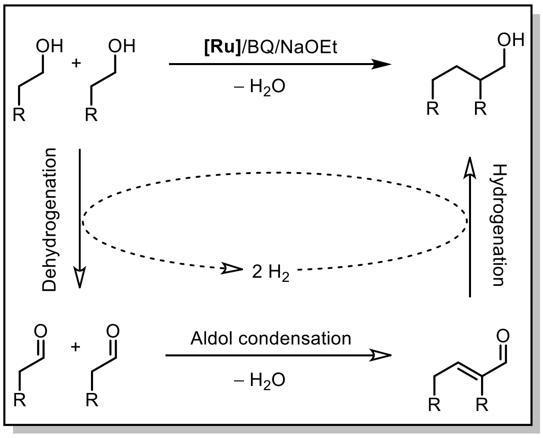

Figure 1. Ethanol homologation directed by the synergistic [Ru]/benzoquinone/base system.

The catalytic system is water tolerant and its reactivity can be extended to bio-ethanol from waste (e.g. a real matrix from head and tail waste from alcohol distillation) toward the production of second generation bio-fuels or lubricants. The catalytic [Ru]/BQ diad is prone to be recycled.[2]

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Ad hoc O3A

FROM MONONUCLEAR TO DINUCLEARCHROMIUM(III) COMPLEXES WITH-[OSSO]-TYPE LIGANDS FOR THE ROCOP OF EPOXIDES WITH CO_2 AND ORGANIC CYCLIC ANHYDRIDES

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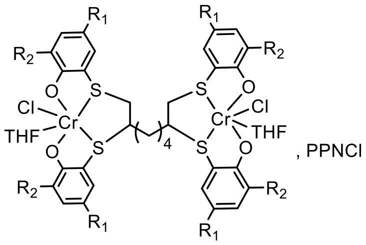
Carbon dioxide (CO_2) has been used as a nontoxic, abundant, and inexpensive C1 feedstock for polymer synthesis since the discovery of epoxide/CO_2 copolymerization by Inoue et al. in 1969 [1]. CO_2-based polycarbonates, which are mainly synthesized from the ring-opening copolymerization (ROCOP) of epoxides and CO_2, are biodegradable materials with widespread use in membranesynthesis, drug delivery,and as thermoplastic elastomers [2]. The design of efficient metal catalysts with the help for the selective coupling of epoxides and carbon dioxide has received increased attention over the past decade.
In this study, we introduce new types of dinuclearCr(III) complexes (**1-3**) bearing the *ortho*-, *para*-aryl and -alkyl substituents on bis-thioether-diphenolateproligands. The catalysts in combination with nucleophile Bis(triphenylphosphine)iminium chloride (PPNCl) as co-catalyst were utilized in catalytic CO_2/epoxide copolymerization. In catalytic system of **1**, selectivity toward the polycarbonate was higher than 98% in the cases of Propylene oxide (PO), Cyclohexene oxide (CHO), and 4-Vinyl-1-cyclohexene 1,2-epoxide (VCHO). For 1-Hexene oxide (HO), conversion of 79% and selectivity of 74% was observed toward poly (1-hexene carbonate) by using **1**. Polyester-*b*-polycarbonates were synthesized during catalyticterpolymerization of CO_2/epoxide/phthalic anhydride (PA) for **1** and **2**for all epoxides. Moreover, the kinetic study of formation of poly(propylene carbonate) by **1**/PPNCl as catalytic system was investigated with in situ Attenuated Total Reflection Infrared (ATR-IR) spectroscopy. The kinetic equation was found to be $k=v.[1][CO_2]/[PPNCl]$.[2]



	R1	R2
1	$C(CH_3)_3$	$C(CH_3)_3$
2	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$
3	CH_3	CH_3

Figure 1. *Dinuclear chromium(III) complexes 1-3:*

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Ad hoc O4A

PHOTOCATALYTIC GENERATION OF SOLAR FUELS AND COMMODITY CHEMICALS

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This talk will describe two separate strategies to photocatalytically produce (i) CO from CO_2,[1] and (ii) polymer-grade ethylene from an ethylene feed with acetylene contaminant.[2] CO_2 reduction is accomplished in pure water with an unprecedented combination of performance parameters: turnover number (TON(CO)) >80,000, quantum yield (QY) >3% and selectivity >99%, using $CuInS_2$ colloidal quantum dots (QDs) as photosensitizer and a Co-porphyrin catalyst. The amine/ammonium-terminated ligand shells of the QDs are responsible for the exception performance of this system by establishing (i) an electrostatic assembly with Co-porphyrin, which allow the colocalization of protons, CO_2, and catalyst at the QD core that serves at the source of the electrons; (ii) a dynamic equilibrium between carbamic acid and free CO_2 that increases the local concentration of available CO_2; and (iii) “second-sphere” effects that improve the efficiency of the Co-porphyrin catalyst. (Figure 1A).[1] In a separate system based on a Co-porphyrin catalyst, acetylene is reduced to ethylene, an intermediate in the production of ~50-60% of all plastics. Our system reduces acetylene into ethylene with several advantages over the present hydrogenation technology, including (i) operation with near 100% conversion in an ethylene-rich gas feed and ≥99% selectivity under both non-competitive (no ethylene co-feed) and competitive (ethylene co-feed) conditions, the latter being industrially relevant; (ii) operation at room temperature using light and water in place of high temperature and an external H_2 feed, and (iii) use of cobalt in the catalyst in place of precious metal catalysts (Figure 1B). These features offer substantial advantages over current hydrogenation technologies with respect to selectivity and sustainability.[2]

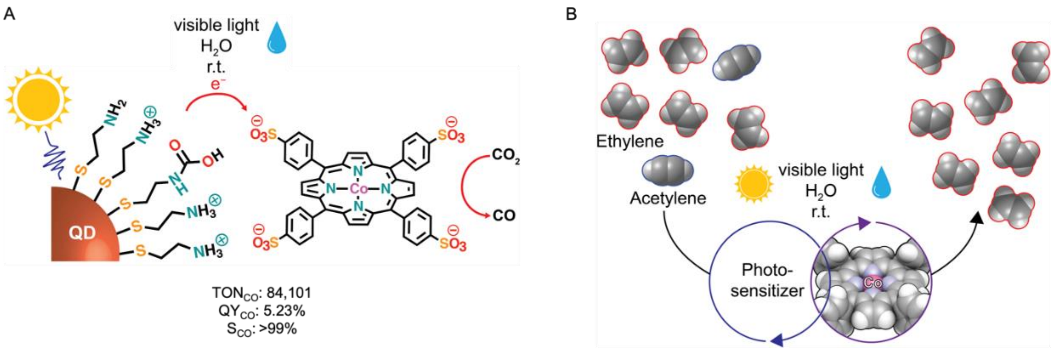

Figure 1: *Photocatalytic reduction of (A) CO_2 to CO and (B) C_2H_2 to C_2H_4.*

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[2] F. Arcudi et all, *Nature Chemistry* **2022**, *14*, 1007–1012.

Ad hoc O5A

EXPLORING MAGNETO-CHIRAL DICHROISM INMAGNETIC MOLECULAR MATERIALS

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Magneto-Chiral Dichroism (MChD) is a fascinating but scarcelyinvestigated manifestation of light-matter interaction specific of chiral magnetizedsystems. It features an unbalanced absorption or emission of unpolarized light thatdepends on the relative orientation of the appliedmagneticfield and the light wavevector and the absolute configuration of the system.[1,2] Its relevance isrelated to potentialtechnological applications, such as the opticalread-out of magnetic data, and its possible implication as a mechanism for the emergence of molecularhomochirality.

Withthis communication I willprovide an overview of the mostrecentresultswe have achieved on this topic, that are aimed at understanding the microscopicparameters and the chemicalingredientsthat are key to observe strongMChDresponses. I willpresent the MChDobserved up to ca. 40 K in a chiral ferrimagnetwith a high $T_C$based on Mn^{II} and Cr^{III} ions,[3] the key-role of spin-orbitcoupling in drivingMChDsignals in a single-chain magnet based on tetragonallydistortedMn^{III} ions (Figure 1),[4] and the strongMChDobserved for two chiral Yb^{III}-helicene complexes detected by near-infrared light absorption.[5]Finally, I willpresent the first comparisonbetweenexperimentalMChDspectra and thosetheoreticallycalculatedthrough quantum chemicalcalculations, showing the fundamentalrole of vibroniccoupling in enhancing the intensity and determining the shape of the MChDsignals of chiral Ni^{II} complexes.[6]

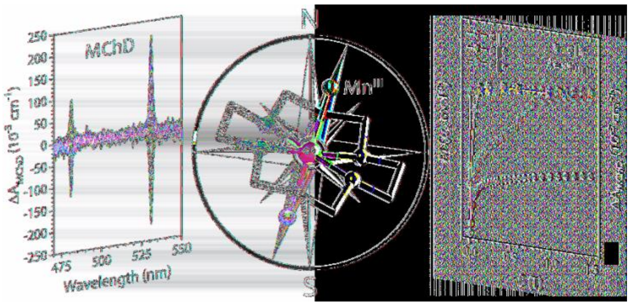

***Figure 1**: View of a portion of the molecular structure of the investigated Mn^{III} 1D chiral compound (middle), corresponding MChD signals observed by irradiation with visible light in a magnetic field (left) and comparison between optical and magnetic data.*

***Acknowledgements**: The French National Research Agency (ANR) is acknowledged for financial support through MONAFER (ANR-18-CE09-0032) and MACHINACO (ANR-19-CE09-0018) projects.*

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Ad hoc O6A

OPTIMIZING THE MAGNETIC PROPERTIES OF MACROCYCLIC Gd(III) COMPLEXES THROUGH COORDINATION CHEMISTRY

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Over recent years, two major challenges have emerged to the use of Gd^{3+} chelates as contrast agents in magnetic resonance imaging (MRI). The emergence in the early 2000s of nephrogenic systemic fibrosis (NSF) in patients with compromised renal function who had undergone contrast-enhanced MRIs raised concerns over the safety of Gd^{3+} chelates. The use of contrast agents in MRI is also causing pollution. Gd^{3+} is detectable in some drinking water sources as well as in marine life.[1]

A common solution can be applied to both of these problems: reduce the amount of Gd^{3+} administered for an MRI exam while retaining its diagnostic efficacy (relaxivity). The Gd^{3+} chelates used as MRI contrast agents are notoriously inefficient, requiring high doses. Introducing with complete diastereoselectivity aryl substituents into the α-position of the four pendant arms of GdDOTA chelates has a profound effect on relaxivity.[2] Here, we discuss the results of the ^{1}H and ^{17}O NMR relaxometric study applied to Gd^{3+} chelates of two aryl-substituted DOTA derivatives: GdDOTFA and GdDOTBA (Figure 1). The high relaxivity values of the two chelates are associated with their favourable electronic relaxation properties and improved water exchange kinetics, more or less optimal to achieve the highest relaxometric performances.[3-4] The α-benzoate substituents of GdDOTBA lead to an increase in relaxivity of two-three times in comparison to that of current agents, which is maintained across the field range 0.5 to 3.0 T. Furthermore, both chelates, due to the presence in the structure of aromatic moieties, can effectively interact with human serum albumin, thus generating supramolecular adducts with restricted tumbling motion and high relaxivity values at the clinical magnetic fields. Outstanding results have been obtained for GdDOTFA: aromatic α-phenyl substituents of the complex permit binding to human serum albumin that slows tumbling, increasing relaxivity to a maximum value of 110 $mM^{-1}s^{-1}$, close to the theoretically maximum value achievable for a monohydrated Gd^{3+} chelates.

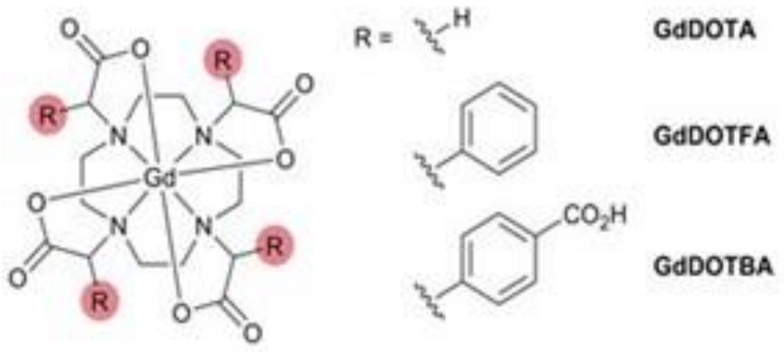

***Figure 1**. The structures of the Gd^{3+} chelates of DOTA, DOTFA and DOTBA.*

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Ad hoc O1B

LANTHANIDE-BASED NEAR-INFRARED AND MULTICOLOR EMITTERS FOR PHOTONIC INTEGRATED CIRCUITS AND QUANTUM OPTICS

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[3]*Institute of General and Physical Chemistry, Belgrade, Serbia*
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Optical and photonic systems are nowadays at the heart of modern technology towards sustainable and energy-efficient devices for computing, communication, data security, including linear photonic integrated circuits and the newly emerging frontier of quantum optics. The high color pure and long lived emission delivered by the lanthanide f-f transitions establishes a unique value for the realization of such devices, which require efficient near-infrared optical output but also the opportunity for wavelength tunability allowing for signal multiplexing.

In this contribution, we show how controlling the multi-step emission photocycle in organically-sensitized lanthanide based systems is an exceptional opportunity for achieving efficiency enhancement and light color tunability. By tailoring the chemical nature, shape, geometry, size and electronic density distribution of the organic sensitizer, highly efficient dye-sensitized multi-layered nanoparticles with multimodal upconversion/downshifted emission[1-2] and dual near-infrared and mechanochromictunable visible orange-to-panchromatic white light emission in a dysprosium single molecular complex have been realized.[3] Finally, we propose such materials as a new paradigm in single-photon generation for quantum optics (EIC Pathfinder Challenges "ARTEMIS" GA 101115149).

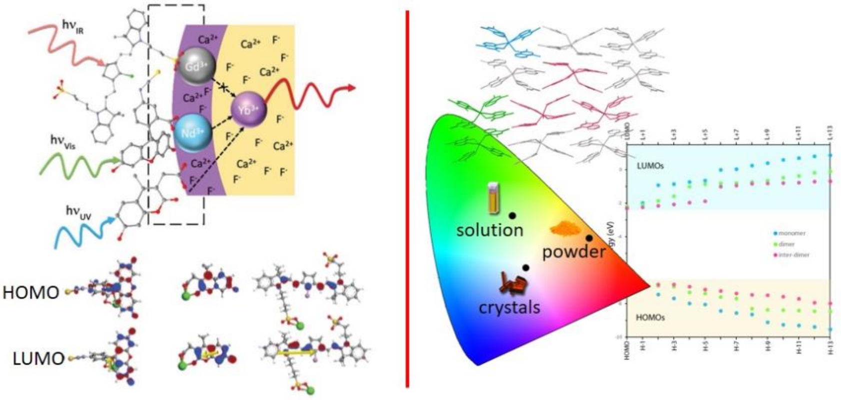

Figure 1: *Ln^{3+}dopedlayerednanoparticleswiththreedifferentdyes. Right. electroniclevels and CIE diagram for a Dy^{3+} single-moleculemechanochromicemitter.*

Acknowledgements**:** *EC H2020 Marie Skłodowska-Curie Action and FWO – Research Foundation Flanders (No 665501 and Travel Grant V506423N) are gratefullyacknowledged for partlysupportingthisresearch.*

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Ad hoc O2B

INTERACTION BETWEEN HEMIN AND NEURONAL PEPTIDES RELEVANT TO NEURODEGENERATIVE DISEASES AND BIOINSPIRATION FOR ROS REGULATION

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Heme is essential for many physiological processes, acting as a prosthetic group of proteins and enzymes involved in oxygen transport, electron transfer, enzymatic reactions that requires oxygen activation.[1] Moreover, it has also an important role as intracellular messenger.[2] On the other hand, free heme is highly toxic because of its potential oxidizing and nitrating properties. For this reason, heme homeostasis dysregulation can contribute to several pathologies such as neurodegenerative diseases, vascular disorders, cancer, or severe hemolysis and is also relevant under conditions of heavy heme release occurring, e.g. on traumatic brain injury.[3]

Our research group investigated the binding and reactivity of ferric heme (hemin) and peptide fragments of proteins involved in neurodegeneration. For instances, histidine residues present in amyloid beta (Aβ), tau protein and prion protein allow hemin coordination with moderate affinity.[4-7] In general, we observe that binding affinity is enhanced by increasing the number of histidine residues. The peroxidase-like activity of the hemin-prion peptide complexes and hemin-induced aggregation were also evaluated. Giving to the importance that reactive nitrogen species (RNS) has on neurodegeneration, we have recently extended our interest on nitrative reaction promoted by hemin-Aβ16 complex.[8]

We are also extending the previous study of hemin-Aβ interaction to related metal-macrocyclic complexes with similar capability to promote oxidation and nitration of Aβ peptide. Our current interest thus focuses on expanded metalloporphyrins known as texaphyrins, which capable of deactivating ROS and RNS. Mn-texaphyrin has been probed to drastically reduce the oxidation and nitration of Aβ.[9] This compound then seems to be promising for its use as a therapeutic agent, since it would be able to reduce cellular damage associated with ROS/RNS in this and perhaps other neurodegenerative diseases. The properties of other Mn-texaphyrin complexes and Mn- and Fe-corrole complexes were also investigated to devise new therapeutic agents against oxidative stress.

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Ad hoc O3B

UNVEILING THE MECHANISM OF ACTION OF MEDICINAL INORGANIC COMPOUNDS: INTERPRETATION, CHALLENGES AND FUTURE DIRECTIONS

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Metals have been extensively used in traditional medicine since centuries, with a leading role. Though, it has been possible to rationalize the beneficial effects of inorganic drugs -from a mechanistically-oriented point of view- much later. Nowadays, thanks to the available technologies and to the modern multiomic strategies, this approach has been functionally developed and implemented. Accordingly, it has been possible to ascertain that a unique biological target for the pharmacological effects of metallodrugs -and inorganic drugs in general- is unlikely to exist. In this context it is here proposed an overview on some integrated and multi-techinique approach capable to unveil the molecular interactions underlying the biological effects of metallodrugs.[1] It is also highlighted how, the obtained information, may turn relevant for applications different from mechanistic studies. For instance, approved metallodrugs for which it has been ascertained the ability to bind specific aminoacidic residues of various proteins, can be conveniently exploited for solving problems related to protein structural resolution.[2] Eventually, it will be presented a case study in which an unprecedented palladium/arsenic-mediated catalytic cycle for nitriles hydration, has been serendipitously discovered thanks to the previous studies on As_2O_3 (Trisenox®) and its arsenoplatin derivative AP-1.[3,4]

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Ad hoc O4B

COPPER AND ZINC MOFS AT WORK: FROM SENSORS TO BIOMEDICAL APPLICATIONS

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In this presentation we will first describe the synthesis and characterization of a novel copper-based Metal-Organic Framework (MOF) labelled Cu-YBDC (where Y stands for alkYne and BDC for benzene dicarboxylate) functionalized witha new linker, a 5-substituted isophthalic acid bearing a propargyl carbamate groupintended to provide a support for gold species for sensoristic applications.[1-3]

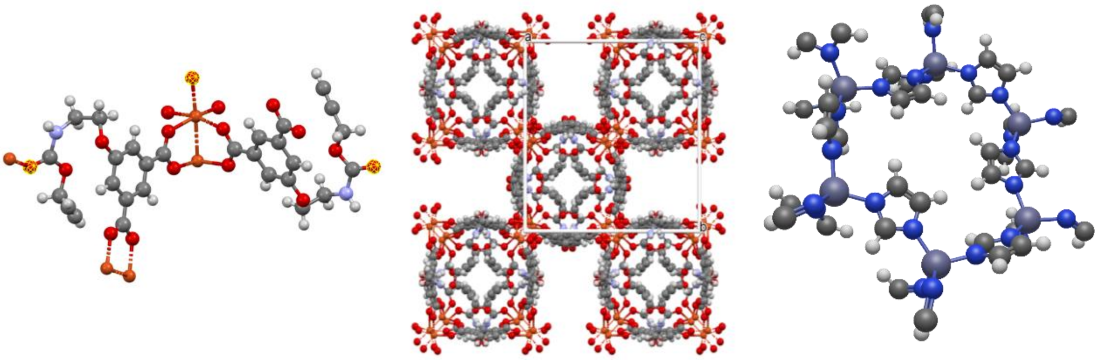

***Figure 1. Left**: the paddlewheel moiety of Cu-YBDC. **Centre**: the Cu-YBDC crystal packing. **Right**: ZIF-8.*

The electrochemical properties of Cu-YBDC were investigated immobilizing it on a Glassy Carbon electrode by drop-casting (GC/Cu-YBDC). Afterward, GC/Cu-YBDC was decorated by Au nanoparticles and the resulting GC/Au/Cu-YBDC electrode has been tested as a nitrite sensor, exhibiting an enhanced electrochemical nitrite detection, with a calculated LOD of 5 μM, significantly lower than the maximum nitrite concentration allowed by the WHO in drinking water. In the second part we will describe our ongoing work with Zeolitic Imidazolate Framework-8 (ZIF-8) a subclass of MOF formed by the self-assembly of zinc ions and 2-methylimidazole. ZIF-8 has attracted considerable attention due to its high thermal and moisture stability compared to other MOF structures. It shows excellent biocompatibility, stability under physiological conditions and responsiveness to the weak acidic environment associated with malignant tumors and other diseases.

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Ad hoc O5B

RUTHENIUM(II) POLYPYRIDYL COMPLEXES AND LIGHT: A POWERFUL COMBINATION IN THE DESIGN OF PHOTORESPONSIVE BIOACIVE COMPOUNDS

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Photodynamic therapy (PDT) continues to attract increasing interest due to the important chance to a achieve a precise spatio-temporal control over the drug activation of several potential antitumoral and antibacterial agents.[1] In this scenario, Ru(II)-polypyridyl complexes (RPCs) represent an intriguing and versatile class of compounds, whose rich chemical-physical repertoire makes them ideal candidates as photosensitizers (PSs) for PDT. An attractive side about their use in this field of research consists in the possibility to incorporate optimally designed ligands in their octahedral geometries, with the goal to tune or maximize some important characteristics for their behavior as PSs. In this work, the influence imparted by the incorporation of these ligands on the photochemical and photobiological properties of the resulting PSs will be presented and discussed.

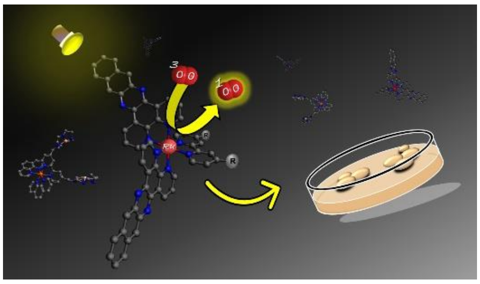

***Figure 1**: RPC are versatile tools in the development of new PDT agents.*

Our analysis will start from the employment of polyamino macrocycles-based chelates to develop highly charged RPCs, which can be used directly in aqueous media, a fundamental prerequisite for their biological application, and possess augmented abilities to interact with key biological targets (such as DNA and protein).[2] Other important features that a PS should possess are the ability to efficiently sensitize the formation of cytotoxic species and to display higher molar absorption coefficients in the red. To this aim, a second class of complexes, featuring the simultaneous presence of two of the popular π-expansivebenzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppn) ligand in the same scaffolds were synthesized by our group.[3] Lastly, prompted by the same object, we also explored the effects deriving from the Ru(II)-coordination by phenanthroline units fully conjugated with additional chromophores, resulting in challenging bichromophoric systems for PDT.

The object of this work is to demonstrate the potential and the opportunities that may arise from the application of this versatile and attractive class of compounds in the drug discovery of novel PSs for PDT.

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Ad hoc O6B

UPCONVERTING NANOPARTICLES FOR ADVANCED FRET BIOSENSING AND BIOIMAGING

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Rare earth doped upconversion nanoparticles (UCNPs) can convert near-infrared excitation into visible emission, leading to background-free photoluminescence.[1] This unique photophysical feature of UCNPs is ideally suited for Förster resonance energy transfer (FRET) based biomedical probes.[2] However, despite numerous advances in synthesis procedures, NP sizes, sensitizer/activator ratios, rationalization of upconversion mechanism[3] etc., identifying the ideal UCNP configuration for real-world applications is everything but trivial, especially for implementation into Förster resonance energy transfer (FRET) based biosensing and bioimaging. FRET is a strongly distance-dependent mechanism that only occurs within 1 to 10 nm donor-acceptor distance range, therefore, a careful design of UCNP FRET systems, including their surface bioconjugation, is paramount for developing efficient biosensors that can fully exploit the photophysical properties of UCNPs. In this contribution, I will discuss our recent work on the optimization of a Nd^{3+}, Yb^{3+}, Er^{3+} - doped $NaYF_4$ UCNPs toward FRET biosensing, including UCNP architectures, specifically designed surface coatings, and their implementation into DNA and RNA FRET based biosensing, and imaging in cells.

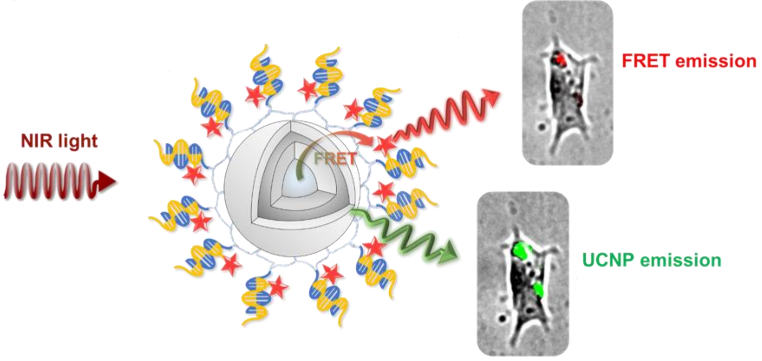

***Figure 1**: Scheme of UCNP FRET based biosensor.*

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ORAL COMMUNICATIONS

OC1A

METAL SUBSTITUTION AND AGGREGATION OF COINAGE METALS CYCLIC TRINUCLEAR COMPOUNDS, DRIVEN BY NEAT METALLOPHILICITY

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An ongoing study on coinage metal Cyclic Trinuclear Compounds, CTCs, promotes them as smart-materials with sophisticated applications in the field of sensors and for the construction of OLEDs.[1] Moreover, charge-transfer and/or stacked complexes based on self-assembling CTCs into long-ordered, well-defined stacks can be envisioned as materials for a bottom-up design of p-n junctions on the molecular level.[1]The nature of intermolecular non-covalent interactions highly influences the final supramolecular architectures, and CTCs of coinage metals are adopted as the building blocks through the chemical modifications of metal, ligand, and substituents. Supramolecular charge transfer adducts can be prepared by mixing CTCs with purely organic donor/acceptor compounds[2] or with complemental donor/acceptor CTCs.[3] Previous studies have detailed that these latter afford ordered charge-transfer stacked complexes, giving rise to shortened intertrimer Au–Ag distance of 2.868(2) Å and larger binding constant up to 4.67×10^5 L/mol.Moreover, mixing solutions of CTCs bearing different ligands and metals allowed the formation of mixed metals/mixed ligands CTCs with the shortest ligand unassisted Cu-Au never attained (2.8750(8) Å), displaying bright photoluminescence and near-unit quantum yields.[3] In this work, we approached an almost clean hetero-metallophilic control for the preparation of stacked heterobimetallic CTCs materials, featured by Ag_2Au or Au_2Ag metal frameworks, whose formation is given by pure closed shell d^{10}-d^{10} interactions, achieving visible light emission enhancement. The final Ag_2Au or Au_2Ag CTCs, exhibit shorter intra-and inter-trimer M-M bond distances than those found in the original starting CTCs.

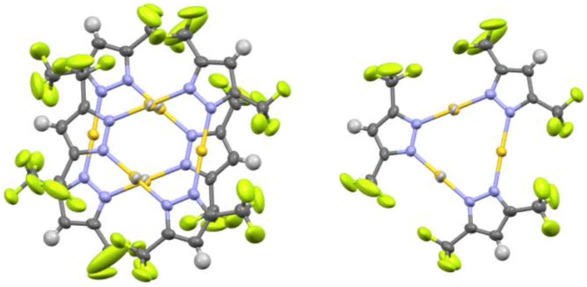

***Figure 1**: Views of the packing unit (left) and of the crystallographic unit (right) for [$Ag_2Au(\mu$-N,N-3,5$(CF_3)_2$pyrazolyl$)_3$]*

***Acknowledgments**: R. G. acknowledges the National Science Foundation (CHE-1413641 and an international supplement thereof, CHE-1545934).*

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OC2A

NEW TRIIRON COMPLEXES VIA INCORPORATION OF ISOCYANOFERROCENE IN A DIIRON SCAFFOLD

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Since the pioneering research by Pombeiro and Fischer, aminocarbyne ligands have appeared in the literature in combination with a variety of transition elements and complex nuclearity.[1] They offer many possibilities for the construction of unusual organometallic structures. In this work, the synthesis of the first N-ferrocenyl (N-Fc) aminocarbyne complex (**1**) was achieved on a diiron bis-cyclopentadienyl scaffold via incorporation of isocyanoferrocene (Figure 1). The {CN(Fc)Me} fragment possesses a hybrid aminocarbyne-iminium character, and the ferrocenyl moiety induces unusual steric and electrochemical features with respect to related diiron complexes.[1a,2] The structural features, electrochemical properties, and reactivity of **1** to afford a series of triiron derivatives (**2-3**) will also be discussed, together with the potentiality of the new complexes as anticancer drug candidates.

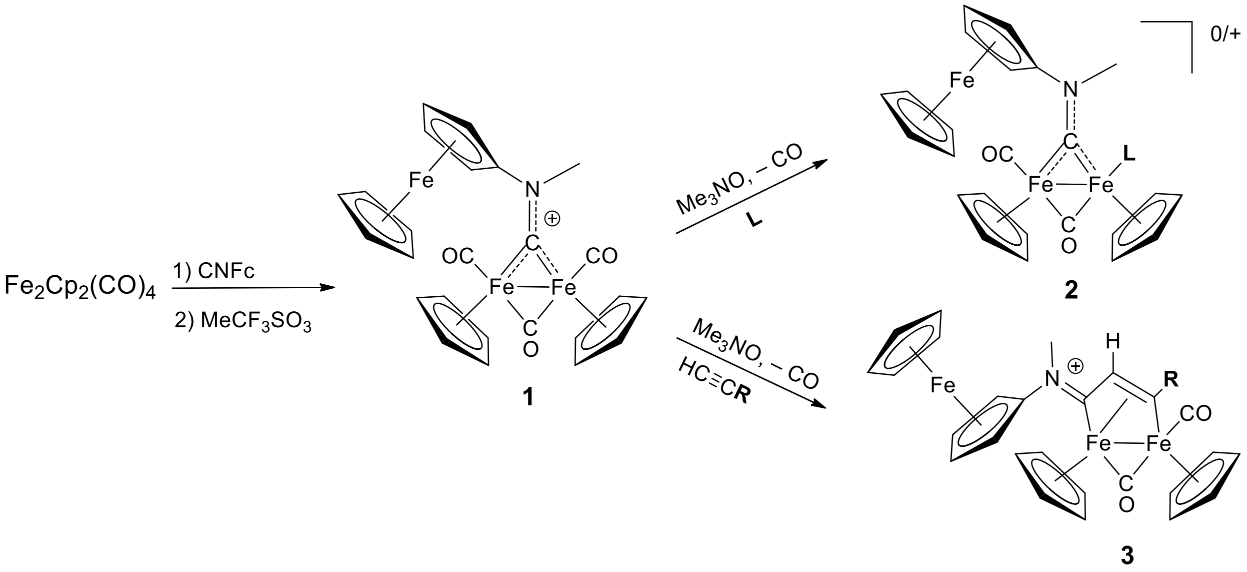

***Figure 1**: New diiron complexes (triflate salts) with bridging N-ferrocenyl hydrocarbyl ligands.*
L = CN(C_6H_{11}), CN(4-C_6H_4OMe), CNMe, NH_3, Cl; R = Me, Ph.

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OC3A

COORDINATION EQUILIBRIA IN HOMOLEPTIC COPPER(I) COMPLEXES

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The ability of Cu to switch between its two main oxidation states is exploited in many natural processes and has important application in different fields dealing with redox processes, such as dye-sensitized solar cells, solid-state lighting devices, and redox-active catalysts.[1,2] Inspired by nature, chemists are learning how to manage the Cu^I/Cu^{II} redox couple. Indeed, to be effectively exploited, Cu needs to be conveniently stabilized by molecular ligands or supramolecular structures.

In this contribution, we present a series of homoleptic copper(I) complexes based on N^N bidentate substituted 1-(pyridin-2-yl) imidazo[1,5-*a*]pyridine ligands. These compounds have been synthesized and their structural and electronic properties investigated by means of a multi-technique approach and rationalized as a function of the steric and electronic effects of the differently hindered ligands.

The collected data unveil very peculiar electrochemical features, attributable to the presence of coordination equilibria between different coordination forms that coexist at room temperature and are resolved by decreasing the temperature. The obtained results have fundamental implications to define the processes involving the change of geometry and oxidation state of the Cu^I/Cu^{II} redox couple; a hot topic in literature, with implications in different fields.

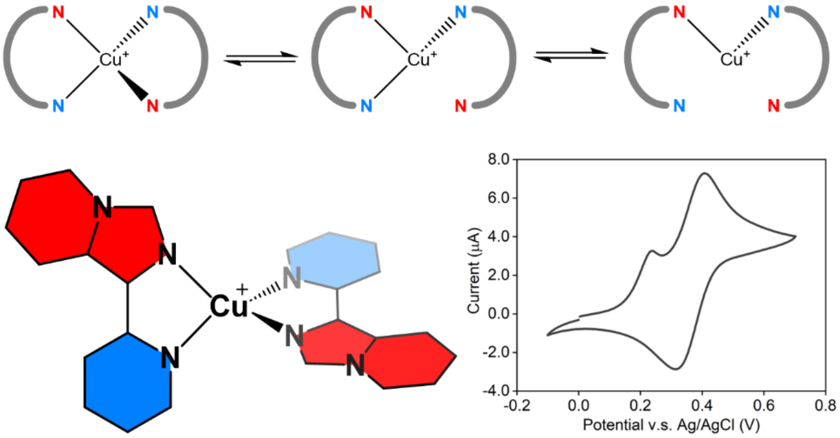

Figure 1*: schematic representation of coordination equilibria and electrochemical properties.*

Acknowledgements*: Authors acknowledge support from the Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023-2027" (CUP: D13C22003520001).*

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OC4A

SYNTHESIS AND BIOLOGICAL INVESTIGATIONS ON RUTHENIUM COMPLEXES BEARING PYRROLE DERIVATIVES

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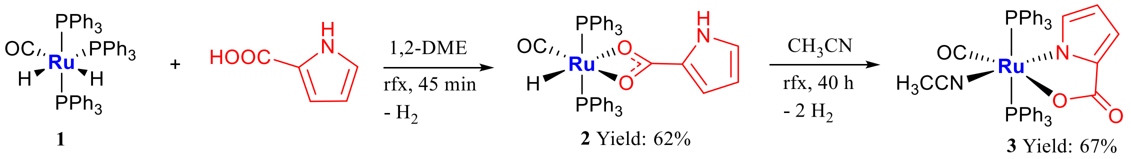
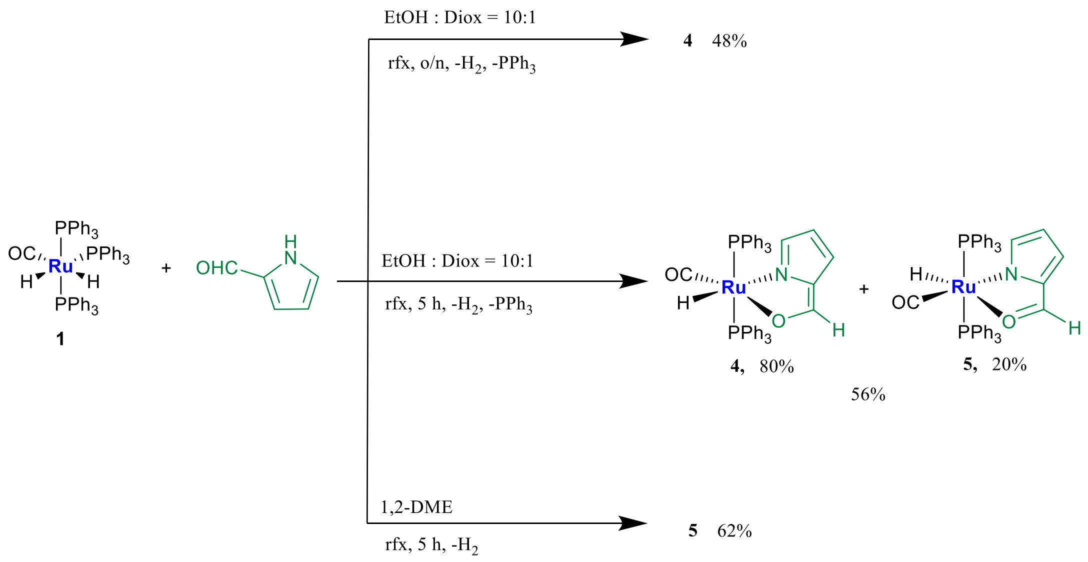
A series of Ruthenium compounds, which contain pyrrole 2-carboxylic acid (HL_1) or 2-pyrrole carboxaldehyde (HL_2), have been selectively synthesized. The reaction between $[Ru(H)_2(CO)(PPh_3)_3]$, **1**, and HL_1 results in the formation of homoleptic k^2(O,O)-$[Ru(H)(CO)L_2(PPh_3)_2]$, **2**. Thus under prolonged CH_3CN refluxing treatment, compound **2** undergoes a transformation, leading to the stable neutral solvento-pyrrolide species k^2(N,O)-$[Ru(CH_3CN)(CO)(L_1))(PPh_3)_2]$, **3** (scheme 1). This transformation promotes an unusual conversion from O,O- to N,O- chelate fashion mode.



Scheme 1. *Syntheses of complexes 2 and 3*

On the other hand, the reaction between **1** and HL_2 yields two distinct diastereoisomers of the type k^2(N,O)-$[Ru(H)(CO)L_2(PPh3)_2]$, namely **4** and **5**. However, by optimizing the experimental conditions, both compounds **4** and **5** have been selectively obtained (Scheme 2).



Scheme 2. *Synthesis of complexes **4-5***

The structures of the pyrrolyl-derivatives have been characterized using single crystal X-ray diffraction, and their purity has been assessed from ESI-MS, NMR and IR analyses. Promising biological activities have been investigated for complexes by antibacterial tests, conducted on Gram-positive and Gram-negative bacteria. Further, detailed information concerning anticancer properties of the complexes have been inferred through antiproliferative tests on human cancer cell lines.

OC5A

IRON(III) CLUSTERS WITH "SHORT" SCHIFF BASE LIGANDS

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Oligonuclear metal complexes have always been attractive thanks for their potential applications as molecular magnets, catalysts, but also simply for their aesthetic appealing. Tetradentate N_2O_2 H_2salben and pentadentate N_2O_3 H_3salmp salen-type Schiff base ligands, derived from the condensation of two salicylaldehydes with arylmethandiamines,[1] possess only one carbon atom between the two donor iminic nitrogen atoms with respect to the two carbon atoms of the well-known H_2salen, and this drives toward the selective formation of oligonuclear metal complexes against mononuclear ones.[2,3]

The reactivity of these ligands is particularly interesting in the case of iron(III), and it will be the main target of this contribution.[3] Isolation of dinuclear or tetranuclear compounds (***Figure 1***) can be suitably guided by the reaction solvent and the position of substituents on H_2salben ligands. The base and the presence of water in the reaction mixture are also crucial point in the reaction with H_3salmp. Crystal structures and the magnetic properties of the most representative cases will be reported.

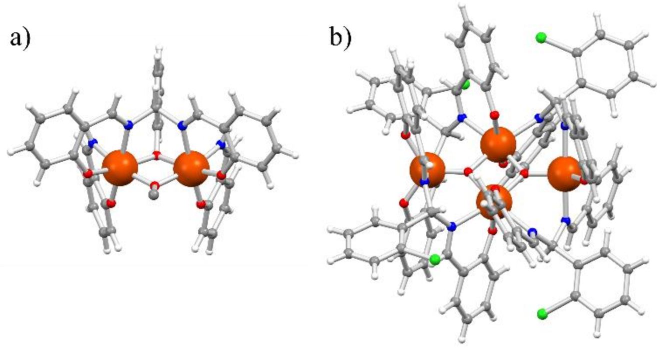

Figure 1: *Crystal structures of a) [Fe_2(μ-salmp)(μ-OMe)(salim)$_2$]·1.5H_2O [3a] and b) [Fe_4(μ_3-O)$_2$(μ-sal(2-Cl)ben)$_4$]·2iPr_2O; [3b] colour code: Fe = orange, Cl = green, O = red, N = blue, C = grey, H = white; co-crystallized solvent molecules were omitted for clarity.*

Acknowledgements: *Dipartimento di Scienze Chimiche e Geologiche of the Università degli Studi di Modena e Reggio Emilia for the funding through the Fondo Dipartimentale per la Ricerca 2021, linea dottorato (FDR 2021).*

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OC6A

4-NITROSOPYRAZOLATE SILVER(I) COORDINATION COMPOUNDS: OLIGOMERIC STRUCTURES HELD BY ARGENTOPHILIC INTERACTION

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Pyrazolate complexes of coinage metals represent an interesting class of coordination compounds characterized by different nuclearity, ranging from polymeric chains to planar trinuclear systems and even less common structure such as saddle-shaped tetranuclear and hexanuclear units.[1]

On the other hand, metallophilic interactions are usually described as occurring in contacts between metal centers in closed shell (d^{10}, s^2) or pseudo-closed shell (d^8) electronic configuration,[2] such as gold(I), copper(I), palladium (II), platinum (II), mercury (II), nickel (II) and silver(I). Such interactions are thought to be important for structural control and self-assembling properties, catalysis,[3] luminescence and sensing.[4]

Herein, a series of thermochromic silver(I) coordination compounds of 4-nitrosopyrazoles will be presented, discussing their synthesis and characterization, with a particular focus on the structural analysis carried out by means of single crystal and powder X-ray diffraction, as well as Hirshfeld surface analysis and DFT calculations.

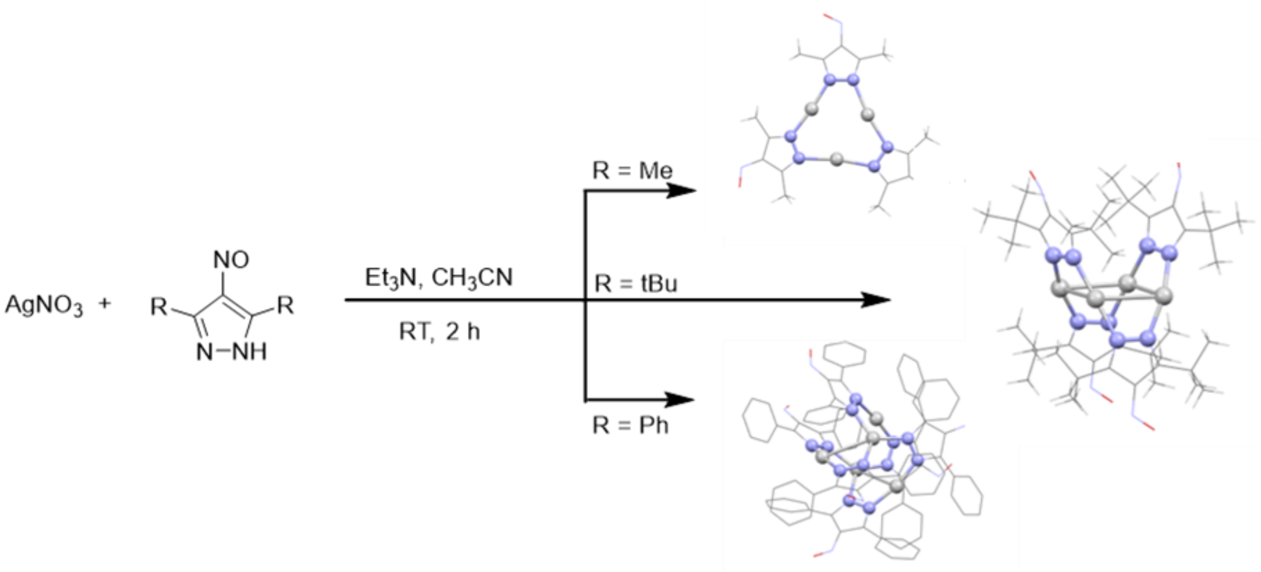

Figure 1: *Synthesis and schematized structures of the compounds presented.*

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OC7A

TWEAKING THE BRIDGE IN METALLOCENE Zr(IV)/W(IV) BIMETALLIC HYDRIDES

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Heterobimetallic zirconocene bridging hydrides form a notable class of compounds, participating in numerous stoichiometric and catalytic reactions.[1] Among several examples, the combination between electropositive zirconocene and nucleophilic metal hydrides is particularly interesting, owing to the complementary electronic properties of the two metals that may enable bimetallic cooperativity.[2] Despite their stability, reactivity of such hydrides towards small molecules has not been extensively studied. Similarly, bonding properties have not been investigated accurately and proper structure-reactivity relationships are not available.

In this contribution,[3] we will report the synthesis of a new class of bimetallic bridging hydrides featuring zirconocenes and the nucleophilic metal hydride Cp_2WH_2. We investigated systematically the bonding situation between the two metals upon ligand variation and their reactivity towards small molecules such as Lewis bases, unsaturated substrates and H_2 (Figure 1). NMR spectroscopy, X-Ray diffraction and DFT calculations have been used to investigate these aspects and to rationalize how different Zr(μ-H)Warrangements affect the spectroscopic properties and bonding in this class of compound.

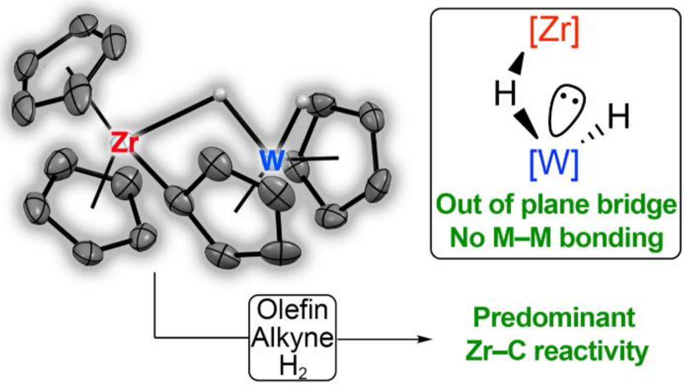

***Figure 1**: Aim of the work*

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OC8A

EXPANDING THE BIOLOGICAL POTENTIALS OF CURCUMIN ANALOGUES AS LIGANDS FOR RU(II) AND OS(II) HALF-SANDWICH COMPLEXES

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Turmeric (*Curcuma longa*) is a plant native to the Indian subcontinent and Southeast Asia that has been used, since the ancient times, as healing agent of medicine for a variety of illnesses. Nowadays is well known that the turmeric is composed by several components and in the last decades many studies established that the curcumin and bisdemethoxycurcumin are important bioactive ingredients. However, its clinical application is restricted by their poor bioavailability due to the low absorption, low hydrophilicity and rapid metabolism. As a result, the research studies are moving towards increasing the curcuminoids bioavailabilitythrough several techniques and the most important is the coordination to a metal center. According to all of this, our research group already studied how the coordination to metals like Ru(II) and Os(II) improves the curcuminoid bioactivity (i.e. anticancer and anti-Alzheimer activities). Herein is reported a new research study where is showed how the modification of the different curcuminoid's functional groups, based on the increasing of their bioavailability, may affect the biological properties of the final Ru(II) and Os(II) complexes. The modifications include aryl side chain bioconjugation (Figure 1a)[1]; reduction of the conjugation's degree (Figure 1b) and heterocyclization of di-keto functionality (Figure 1c). The novel M(II) derivatives containing curcuminoid analogues we report in this work are both neutral and ionic and they also possess different coordination environments according to the presence of either the di-keto functionality or substituted pyrazole ring.

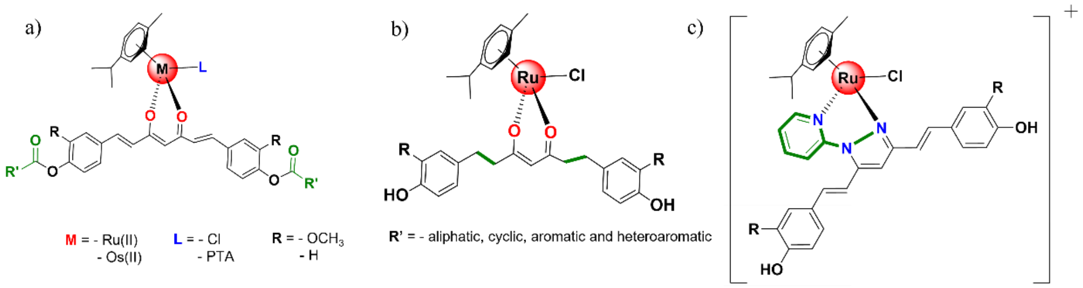

***Figure 1**: Novel Ru(II) and Os(II) organometallic compounds with curcuminoid analogues*

Acknowledgements:

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OC9A

SYNTHESIS AND CHARACTERIZATION OF [IRON(III)(PYCLEN)] AS CATALYSTS FOR OXYGEN ATOM TRANSFER (OAT) AND HYDROGEN ATOM TRANSFER (HAT) REACTIONS

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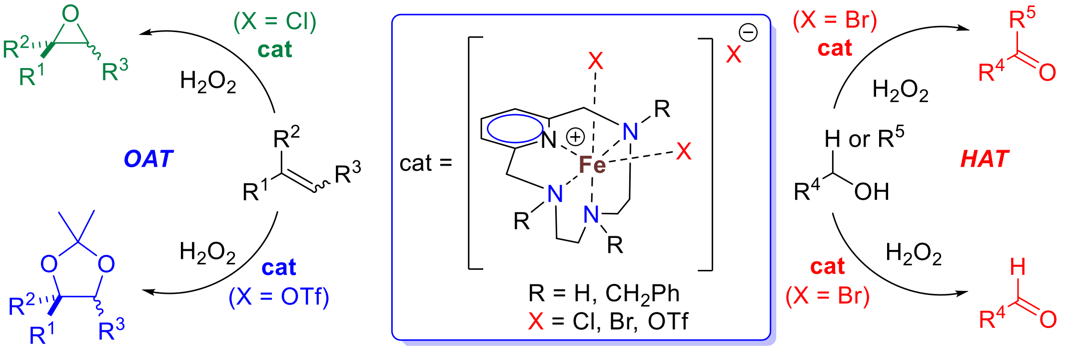
Reactivity of high-valent nonheme iron-oxo complexes in oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions has been shown to be markedly affected by the nature of supporting ligands (*e.g.*poliazamacrocycles) and by the spin state of the iron complex.[1] The introduction of a pyridine moiety into the skeleton of a polyazamacrocyclic ligand affects both thermodynamic properties and coordination kinetics of the resulting metal complexes.[2] These features have engendered a great interest of the scientific community, especially related to the use of those complexes in catalytic oxidation reactions.[3] We report here the synthesis and characterisation of [Fe(III)Pc-L's)] complexes (Pc-L = 3,6,9-triaza-1(2,6)-pyridinacyclodecaphane) and their catalytic applications in stereoselective epoxidation or dihydroxylation reactions[4] and alcohol oxidations[5] using H_2O_2 as the terminal oxidant under mild conditions (Scheme 1). New stable iron(III) complexes with different ligands have been isolated and fully characterized (X-Ray, EPR, ESI-MS, RAMAN), including both mononuclear, binuclear and trinuclear complexes.[6] The oxidation and spin state of the iron centres have been investigated by Mössbauer spectroscopy, macroscopic magnetization measurements and theoretical calculations at DFT/OPBE level. As expected, the structural and electronic features of supporting ligands and anions have a significant effect in the observed and calculated iron spin state, which in turn has a dramatic impact on the studied reactions.



Scheme 1. *Oxidation reactions catalyzed by [Fe(III)Pc-L's)] complexes*

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OC10A

S-BLOCK METAL-CATALYZED HYDROPHOSPHORYLATION OF ALKYNES – FROM BASIC RESEARCH TOWARDS ODDITIES

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Organophosphorus compounds are of utmost importance not only as ligands for transition metal-catalyzed reactions and building blocks in organic synthesis but also in numerous pharmaceutical, agricultural, and material applications and hence the development of alternative efficient methods for their preparation is desperately needed. Hydrophosphorylation reactions, *i.e.* the addition of an H–P(O) bond across an unsaturated system, represent a straightforward and atom-economical pathway to phosphorus-containing molecules but require a catalyst. s-Block metal complexes gained tremendous interest in recent years due to their advantageous properties like non-toxicity and global abundance.[1] A novel approach for the hydrophosphorylation of alkynes with secondary phosphine oxides has been developed using bis(trimethylsilyl)amides of alkali and alkaline-earth metals as precatalysts because these complexes are easily accessible and highly soluble in common organic solvents.[2] The reactivity of the catalyst strongly depends on the softness of the metal ion with rubidium and cesium being the most active congeners. The aryl substituents of Ar_2PHO have been varied, showing that Mes_2PHO leads to metalation of an ortho-methyl group and subsequent formation of a dihydrophosphindole oxide derivative.[3] The variation of the alkyne moiety has paved the way towards novel synthesis methods for an exciting and widely used ligand class.[4]

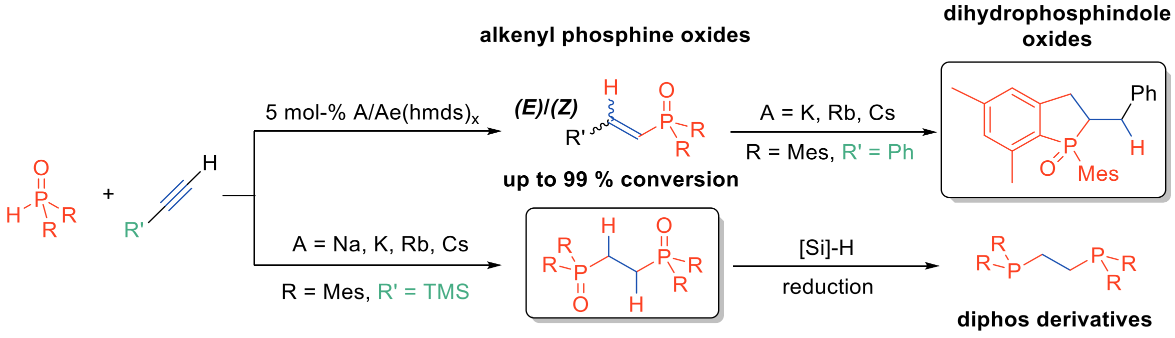

Figure 1*: s-Block metal-catalyzedhydrophosphorylation of alkynes generating alkenyl phosphine oxides and subsequent formation of phosphindole oxide by cyclization reaction. The usage of TMS-acetylene leads to double addition and desilylation forming sterically encumbered diphos oxides.*

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OC11A

FORMIC ACID AS A CO SURROGATE IN PALLADIUM-CATALYZED REDUCTIVE CYCLIZATION REACTIONS OF NITROARENES

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Transition metal catalysed reductive cyclization reactions of suitably substituted nitroarenes to yield heterocycles using carbon monoxide as a reductant have been known for many years. However, their use has not become common among synthetic organic chemists due to the limitations involved in the use of pressurized CO.[1] In recent years, we have developed the use of phenyl formate as a cheap and non-toxic CO surrogate, able to liberate CO under the reaction conditions, thus allowing the same cyclization reactions to be performed in a single glass pressure tube. The system was applied to the synthesis of different *N*-heterocycles.[2-6] However, phenol is formed as a coproduct, which is toxic and can be difficult to separate in some cases. More recently, we were able to employ formic acid, activated by acetic anhydride, as a simpler CO surrogate for the cyclization of *o*-nitrostyrenes to indoles,[7] and here we report our very recent results on the use of this compound to effect the synthesis of oxazines from nitroarenes and conjugated dienes and that of 4-quinolones from 2'-nitrochalcones. In both cases, the reaction is catalysed by a palladium/phenanthroline complex generated *in situ*. Moreover, the dehydration of the formed oxazines to *N*-arylpyrroles was also investigated. After several attempts, we found that the best catalyst to promote this reaction is CuCl.

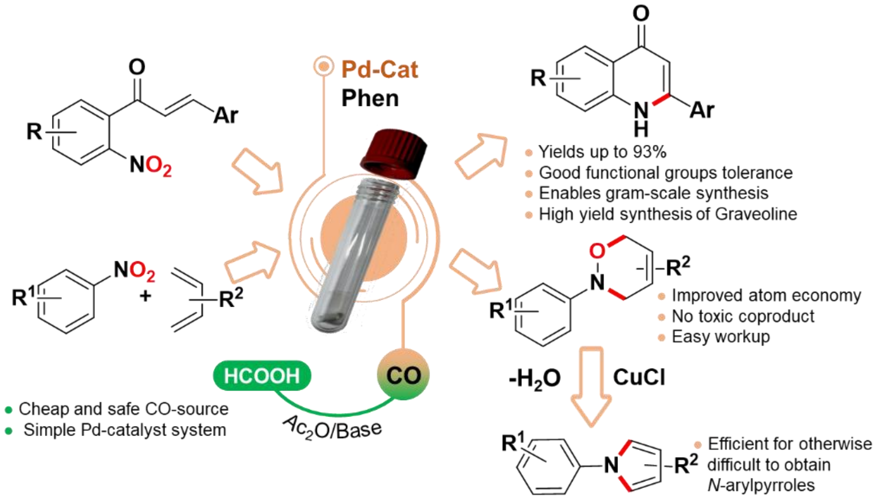

***Figure 1**: New applications of formic acid as a CO surrogate*

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OC12A

ACETONITRILE AS A NOVEL SELECTIVITY ENHANCER FOR THE DIRECT SYNTHESIS OF HYDROGEN PEROXIDE

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Federica Bertelà,[4] Alberto Lopez,[4] Chiara Battochio,[4] Carlo Meneghini,[4] Marco Zecca[1]

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The technological implementation of the direct synthesis of H_2O_2, one of the most investigated topics in heterogeneous catalysis, has been prevented so far by its relatively low selectivity. [1] The best promoters so far (i.e. Cl^- and Br^- ions) are good ligands to Pd(II),[2] but lead to corrosion issues.[3] Acetonitrile (ACN), which is also a good ligand to Pd(II), was reported as an effective co-solvent for this reaction in the H_2/O_2 explosive range.[4] Thus, we investigated it as a non corrosive, inexpensive selectivity enhancer under H_2-lean conditions in a semi-batch reactor at atmospheric pressure (24 mL/min O_2, 1 mL/min H_2) and 25 °C, with a methanol/ACN mixture (90/10, v/v) as the solvent. Two Pd catalysts supported on SSZ-13 zeolite and sulfonic polydivinylbenze (SpDVB) were prepared by ion-exchange and the subsequent reduction with H_2 and compared with a commercial Pd/C catalyst. Whereas the latter is poisoned by ACN, with Pd supported on the ion-exchangers its addition significantly slows down the H_2 consumption without affecting the rate of H_2O_2 production (Pd/SSZ-13) or even increasing it (Pd/SpDVB) (Figure 1). *Ex-situ* XAS of the catalysts shows the increase of the PdO/Pd ratio, which is higher for both when ACN is used as the selectivity enhancer. This higher oxidation degree of Pd in the presence of ACN is confirmed by XPS analysis (Figure 2). This suggests that the oxidation of Pd in the presence of ACN might be facilitated by the formation of cationic Pd(II) complexes. As no Pd leaching is observed, they are arguably retained by the solid ion-exchangers. Their subsequent reduction with H_2 might set up a "release-and-capture" mechanism for the reconstruction of the nanostructured metal, previously observed with TEM for Pd/SpDVB.[5] The ensuing continuous refresh of the metal surface might remove the most active and less selective sites with the eventual enhancement of the selectivity.

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OC13A

STRATEGIES FOR IMPROVING THE PHOTOCATALYTIC PERFORMANCE OF NANOSTRUCTURED TITANIA IN THE VISIBLE RANGE

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Nanosized Titania (TiO_2) is one of the most investigated semiconductors for the photodegradation of pollutant species,[1] also due to its low toxicity and - from a green chemistry point of view - excellent environmental sustainability. The anatase form of TiO_2 features a wide energy bandgap of ~ 3.2 eV,[2] capable of photocatalyze several degradation reactions under ultraviolet (UV) light through mechanisms involving radical species and charge carriers as reaction intermediates. Nonetheless, it is of paramount importance to explore different strategies to enhance the photocatalytic performance under solar radiation, since a relevant part of the solar energy is concentrated in the visible part of the spectrum. Possible improvements of the photodegradation process could involve an optimization of the formation of nanostructured TiO_2 from the starting solution, an increase of the catalytic active area, as well as an enhancement of the radiation absorption in the visible range. To these aims, we followed a modified sol-gel synthesis[3] using natural organic structures, in particular diatom earths, as templating agents, to prepare a so-called "biomorphic" structure, while decorating the TiO_2 surface with Au nanostars[4] to exploit plasmonic surface resonance effects to harvest radiation in the visible range. The effect of additives (*e.g.*, chelating agents) has been also investigated to improve the quality of the TiO_2 deposition. The synthesized material has been characterized by X-ray powder diffraction (XRPD) and scanning electron microscope combined with energy dispersive X-ray spectroscopy (SEM-EDX). Preliminary studies on the photodegradation capability of the prepared samples have been carried out using a dye, namely Rhodamine B, by following its decomposition under a LED lamp emitting in the visible region through absorption spectroscopy.

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OC14A

EXPLORING THE EFFECT OF Sn ADDITION TO Au-BASED CATALYST FOR ALKANE OXIDATION

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Supported gold nanoparticles have shown to be extremely active for many industrially important reactions [1]. However, from an industrial point of view, the increasing interest to environmental issues put the attention on the needing of more efficient processes, new methods for synthesis of nanoparticles and rational use of non-critical metals. The present studies are required to be more focused on cheap, non-toxic and environmentally friendly catalysts. Sn has been selected as earth-abundant metal, still poorly investigated as active component of heterogeneous catalysts [2]. In particular, Au and Au-Sn supported catalysts have been synthesized using Au and Sn metal powders as precursors by the solvated metal atoms dispersion (SMAD) method [3], using a reducible (TiO_2) and a non-reducible (Al_2O_3) metal-oxide as support. The samples have been characterized by TEM, STEM-EDS (Fig. 1) and ^{119}Sn-Mössbauer spectroscopy and tested in cyclohexane oxidation.

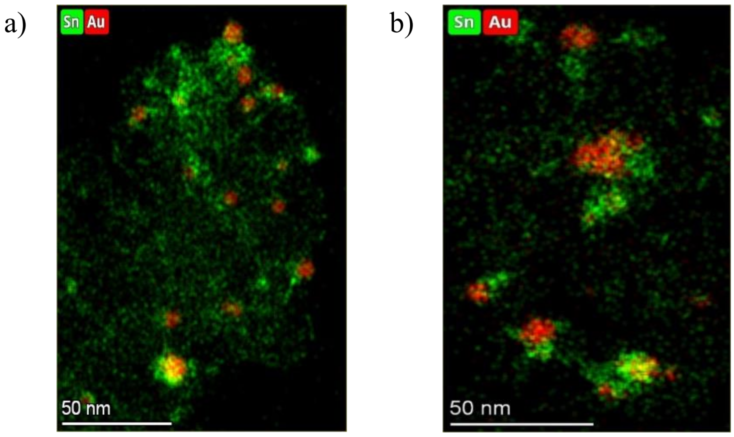

Figure 1. *Au and Sn elemental maps with HAADF image of the Au_1Sn_2/TiO_2 (a) and Au_1Sn_2/Al_2O_3*

The reaction, which is known to proceed through a radical mechanism, has been affected by the support themselves, as they have been proved to act as radical scavenger. The comparison between the supported monometallic and the bimetallic Au-Sn catalysts has allowed to understand the potential role of Sn, which did not impact on the catalytic activity but affected K/A ratio enhancing the formation of K. The effect of SnO_2 appeared to be connected with the enhancement of peroxide formation from molecular O_2.

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OC15A

METAL-EDTA IONIC LIQUIDS CATALIZED CYCLOADDITION OF CO_2 TO EPOXIDES

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CO_2 utilization, as well as carbon capture and storage, have been addressed by an increasing research interest during the last decades. From the viewpoint of *green chemistry* and *atom economy*, the use of CO_2 as a safe, abundant and inexpensive raw material for the preparation of high value chemicals such as organic carbonates, represents a desirable and convenient application.[1-3] Organic carbonates are generally proposed as environmentally friendly solvents, as starting material for the synthesis of polycarbonates, and as gasoline additives.[4]

Ionic liquids (ILs) have been proven to be effective homogeneous catalysts for the synthesis of cyclic carbonates. The use of metal salts (acting as Lewis acids) together with task specific ILs has also been reported, with many catalytic systems displaying interesting performances[5]

Nevertheless, at the best of our knowledge, the use of ILs catalysts featuring metal complexes as part of their structure, in CO_2 cycloaddition reactions (Figure 1), has not yet been reported in literature. In this context, a panel of ILs featuring 1-butyl-3-methylimidazolium cations and metal-EDTA complexes anions has been synthesized and characterized. The correlation between the coordinated metal portion of the IL and its catalytic activity in the cycloaddition reaction of CO_2 to different epoxides has been investigated. The results obtained were then compared with parent ionic liquids with traditional anions and with ILs featuring the same coordinated metal but different ligands. Finally, a computational study was performed in order to rationalize the obtained results.

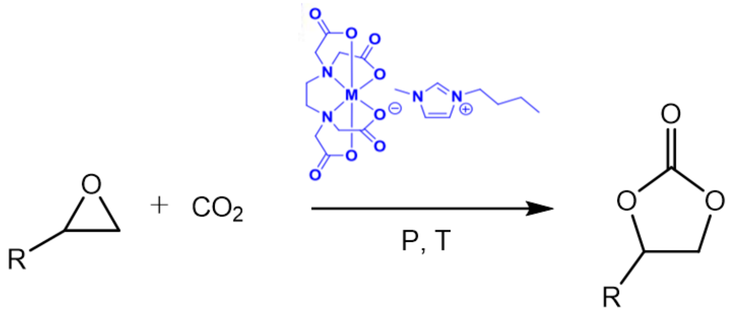

***Figure 1**: Schematic synthesis of cyclic carbonates.*

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OC16A

CATALYTIC ESTERIFICATION OF LEVULINIC ACID WITH POLYOLS

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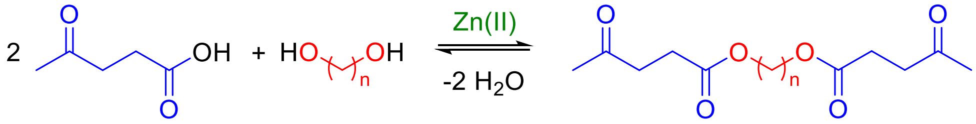
Researchers have recently focused their attention on the conversion and utilization of biomass in response to the growing demand for environmentally friendly chemicals. Among the noteworthy products derived from lignocellulosic biomass is Levulinic Acid (LA), which can be obtained through various methods utilizing raw materials such as glucose, fructose, sucrose, and other sugars.[1] LA serves as a fundamental compound in the chemical industry, primarily functioning as a precursor for pharmaceuticals, solvents, anti-freeze agents, and more.[2] Notably, its esters (LE) are particularly interesting derivatives, finding applications as plasticizers, lubricants, and additives. In industrial formulations, esters of polyols play a significant role as essential components.[3]

The production of LE involves the esterification reaction between LA and alcohols, constituting an equilibrium process accompanied by the formation of water. Typically, the presence of a catalyst is necessary to enhance productivity. Over time, various catalytic systems have been explored, with a growing preference for employing Lewis acids.[4] Zinc(II) salts and complexes have demonstrated remarkable activity in this type of reaction and have gained popularity due to their affordability and biocompatibility.[5] Therefore, in this study, the esterification reaction between LA and polyols was examined utilizing simple inorganic salts of zinc(II) as catalysts (Scheme 1).



Scheme1: *Esterification reaction of levulinic acid with polyols using Zn(II)*

This study incorporated NMR methodology to assess the selectivity formono-esters and di-esters, as well as to monitor the changes in the composition of the mixture during the course of the reaction.

Acknowledgments: *The authors are grateful to Italian Ministerodell'Istruzionedell'Università e dellaRicerca for the financial support provided through the LEVANTE project "LEvulinic acid Valorization through Advanced Novel Technologies", Progetti di Ricerca di Rilevante Interesse Nazionale -Bando 2020, Prot. 2020CZCJN7.*

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OC17A

RECENT ADVANCES IN ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE BY MOLECULAR CATALYSTS FUNCTIONALIZED ON ELECTRODE SURFACE

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The conversion of CO_2 as starting raw material for the production of energy-reach molecules, ideally the so-called efuels, fits two urgent worldwide recognized needs: the concern of the continuous rise of CO_2 concentration in the atmosphere and its environmental consequences, and the longer-term worry for the energy transition from fossil to renewable fuels. Among renewable energy sources, photochemical approaches are of high interest for their direct conversion procedure, but electrochemical methods may take advantages from photovoltaic solar production of electricity, often resulting into a more straightforward and simpler, although strictly correlated, approach. This contribution will deal about the electrochemical reduction of carbon dioxide by molecular catalysts anchored on heterogeneous electrode surface via covalent bonds. Advantages consist into removing the requirement of solubility of the catalyst in the selected solvent, thus allowing to employ water as green and environmentally friend solvent (this is especially important whenever organometallic catalysts are used), as well as greatly enhancing the catalytic stabilities and performances, resulting in Turn Over Numbers (TONs) values that are order of magnitude higher. For example, Mn molecular complexes raised their TON from ≈ 40 to about 162000 when passing from homogeneous (in acetonitrile) to heterogenous system (Mn complex chemically bonded on carbon cloth working electrode and in water as solvent) in gas diffusion layer electrodes.[1] We recently tried to simultaneously overcome the problem of the low carbon dioxide solubility in water and selectivity of the electrochemical reduction products. We demonstrated how utilizing a selected amine (six different amines were employed) dissolved in water can be conveniently used as CO_2 capture system and as co-catalyst for addressing the selectivity. By this approach we passed from CO to formate production with a TON of over 28000. This is especially important from the perspective of real-world applications since direct electrochemical synthesis of liquid efuels are of particular interest. Detailed DFT calculations reveal the molecular mechanism that allow the shift of selectivity from CO to formate production in the presence of the tertiary amine PMDETA (pentametyldiethylenetriamine). In this case, identification of the chemical species in solutions demonstrated that protonation of PMDETA in methanol/water system is the responsible of the observed selectivity shift.[2] Finally, preliminary results on molecular heterogenized catalysts able to convert CO_2 to methanol will also be illustrated.

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OC18A

MECHANISTIC INSIGHTS OF ELECTROCHEMICAL CO_2 REDUCTION CATALYZED BY MANGANESE N-HETEROCYCLIC CARBENE COMPLEXES

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A fundamental understanding of the electrochemical CO_2 reduction reaction (CO_2RR) promoted by transition metal-based catalysts at a molecular level is essential to improve the efficiency and selectivity of the process toward the formation of a specific product.[1] In this regard, molecular electrocatalysts, characterized by well-defined active sites, are ideal platforms to investigate the reaction pathways, through the characterization of the main intermediates.[2]-[3] Since the seminal work by Deronzier and co-workers, tricarbonyl Mn complexes with polypyridyl ligands have been extensively studied as homogeneous molecular electrocatalysts for selective CO_2 reduction to CO.[4] Recently, bidentate N-heterocyclic carbene (NHC) ligands were found to be suitable alternative platforms to classical diimine moieties, showing excellent performances for selective CO_2-to-CO electroreduction in neat non-aqueous media or in the presence of low-to-moderate amounts of water.[5]

In this contribution, we shed light on the main mechanistic features of Mn-NHC electrocatalysts for CO_2 reduction in both aprotic and protic conditions. While the main catalytic pathway results in a highly efficient and selective CO_2-to-CO conversion in aprotic media, a competitive mechanism leading to the catalytic $HCOO^–$ production operates in the presence of weak Brønsted acids. By combining organometallic synthetic chemistry and in situ FTIR spectroelectrochemical (SEC) techniques, we unambiguously characterized the key intermediates involved in the electrocatalytic pathways to CO and $HCOO^–$, respectively, establishing a direct correlation between their formation and the observed selectivity. These findings provide new mechanistic insights towards a fundamental understanding of the origin of selectivity in CO_2RR catalyzed by earth-abundant transition metal-based molecular systems.

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OC19A

EXPLORING THE REDUCTIVE CO_2 FIXATION TO AMINES USING STABLE NHC–PHENOLATE COPPER(II) COMPLEXES

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One of the most important issues that today concerns our society is sustainable development, a goal that humankind must achieve to ensure a future for the next generations. In this context, one of the main challenges is to reduce the concentration of CO_2 in the atmosphere, and one of the most promising approaches involves its capture from energy power plants waste. The high cost related to the capture processes are thereby a limit to the applicability of the method, and several problems are also related to CO_2 storage. The utilization of captured CO_2 as C1 building block for the synthesis of added-value compounds would potentially cover the capture costs and overcome the storage problem.[1] In this frame, the development of new efficient catalysts is important to avoid drastic reaction conditions and to get access to a plenty of different chemical transformations. For this purpose, organometallic metal complexes are great candidates.[2] However, organometallic chemistry was historically focused on rare and expensive late transition metal centers, resulting in active but expensive metal catalysts. In the last years, a renaissance of the organometallic chemistry of Earth-abundant metals is taking place, helped by different features like the metal precursor's cheap price, their biocompatibility, and the capability of undergoing single electron transfer (SET) processes.[3,4] In this contribution, we report our study on the synthesis and characterization of NHC-phenolate copper(II) complexes. The performance of these complexes as catalysts for the reductive fixation of CO_2 with amines, for the synthesis of formamides and methylamines, was also explored (Figure 1).

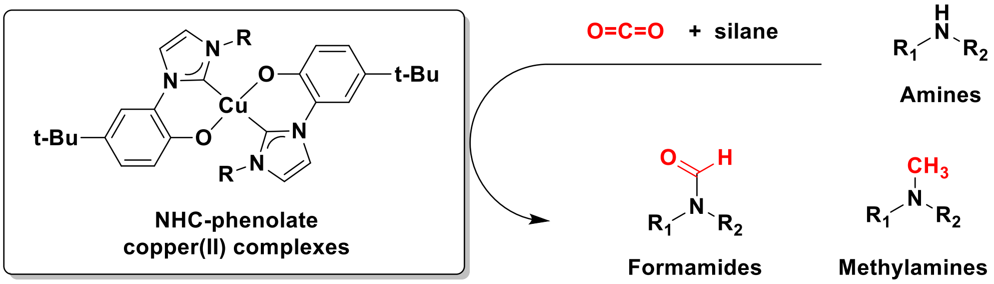

Figure 1

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OC20A

ENABLING COPPER CIRCULARITY: A NEW AGE FOR CO-ORDINATION CHEMISTRY

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The state of the art of copper recovery and refining encompasses three main processes: pyrometallurgy[1], hydrometallurgy[2], solvent extraction[3], and combinations thereof. Copper is extracted primarily from ores, often containing sulphides or oxides[1], resulting in by-products such as sulphur dioxide and hydrogen sulphide, all of which are hazardous and have limited re-use potential. Moreover, copper ores always contain other metals, like Fe, Ni, Zn, As, Sb, Bi, which have to be removed during the process[1]. However, pyro- or hydrometallurgical processes are not extremely selective, and they often require a subsequent solvent extraction step, by means of expensive ligands and kerosene related solvents [3]. Because of this, it is necessary to develop greener and more sustainable approaches based on not hazardous leaching agents and mild reaction conditions.

Herein, we report new insights on copper recovery by hydrometallurgical approaches in mild conditions. The proposed approaches are based on aqueous environments and copper co-ordination chemistry, by systematically varying leaching conditions (e.g. ligand, ligand concentration, time, temperature, pressure) and copper sources. Particular focus was given to the recovery of copper as cupric ion, by exploiting carboxylate complexes and two experimental approaches: a traditional route in flasks, and a novel hydrothermal approach. The recovery of copper from zero-valent copper containing sources (e.g. copper wires, brass) was also addressed, combining the copper coordination chemistry with its redox properties.

In order to assess both the selectivity and the efficiency of the leaching process, and providing a more fundamental understanding of copper reactivity, different analytical techniques were used. In particular, ICP-OES, SEM-EDX and XRD were exploited for elemental and mineral analysis; UV-Vis, FT-IR and TGA contributed to the understanding of copper reactivity and reaction mechanisms.

***Acknowledgements*:**

Manica S.p.a. and PNRR are acknowledged for the financial support

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OC21A

A NEW 2D BLACK PHOSPHORUS-BASED PHOTOCATALYST FOR ENERGY APPLICATIONS

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Photocatalysis has emerged as a promising route for the sustainable production of hydrogen by solar-driven water splitting.[1] However, the four-electron driven half-reaction of water oxidation shows slow kinetics, which, in conjunction with insufficient light absorption and rapid carrier recombination, leads to low solar-to-hydrogen energy conversion efficiency.By optimizing the design and synthesis of photocatalysts, enhanced light absorption, efficient charge separation, and improved surface reactivity have been achieved, leading to significant improvements of the overall performance. Several studies have shown that exfoliated black phosphorus (BP) is a promising candidate in the field of photocatalysis[2] due to its natural semiconducting properties, with a tunable and narrow band gap (from 0.3 to 2.0 eV) that drives the light absorption in the vis-NIR region. High carrier mobility (1000 $cm^2/V{\cdot}s$) and the presence of electron lone pairs on each P atoms that can interact strongly and stabilise transition metals nanoparticles, represent further intriguing properties of this exciting semiconductive material.[3] Here, we report new BP-based nanocomposites with TiO_2 and a metal phosphide as cocatalyst[4] which exhibit a remarkable enhancement of photocatalytic H_2 evolution activity compared to the corresponding bare materials.

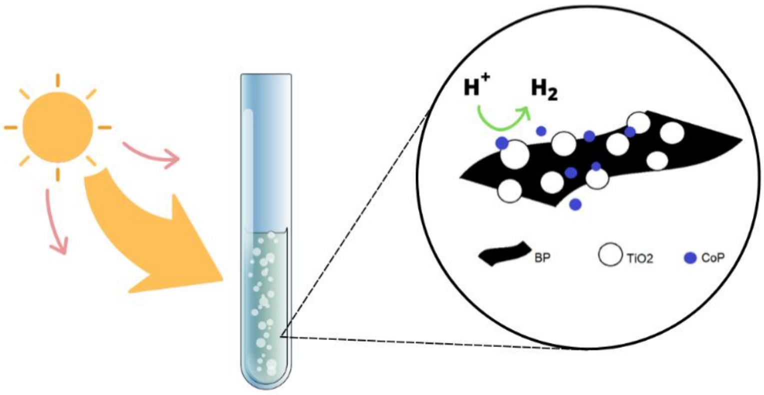

Figure 1*: Photocatalytic hydrogen generation from water using TiO_2/BP/CoP composite under simulated sunlight irradiation*

Acknowledgements**:***This work was supported by MUR with the project PRIN2017KFY7XF and by EC with the Horizon-2020 projects PHOSFUN (ERC Advanced Grant N. 670173) and PHOSMED (ERC POC Grant N. 963933).*

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OC22A

BiOCl/g-C_3N_4 AS AN IMPROVED CATALYST FOR THE ELECTROCHEMICAL REDUCTION OFCO_2 TO $HCOO^-$

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Selective CO_2 conversion to formate is necessary as formic acid is an important feedstock in the chemical industry and could also be used as a fuel in fuel cell[1]. Bismuth-based catalysts have been reported to have good selectivity for CO_2 conversion to formate in numerous works[2,3]. In this work, increased formate production was observed with a heterojunction-based composite. This composite consisted of 52.1% BiOCl/g-C_3N_4 which was noted to have improved formate production ability as compared to the pristine BiOCl. Linear Sweep Voltammetry (LSV) studies were performed in CO_2 and Argon saturated 0.1M $KHCO_3$ electrolyte with a scan rate of 5 mVs^{-1} where an increment in the current density was evident in the LSV curve of the former case. Chronoamperometric analyses were carried out for all the different composites in a three-electrode gas-tight Dr. Bob cell™ connected to an online Gas Chromatography analyzer where the gaseous products were analyzed. The liquid products were analyzed after the Chronoamperometry by an Ionic Chromatography analyzer. Faradaic efficiencies (F.E.) accounted for 70% - 77% of formate production for the different composites and 52.1% BiOCl/g-C_3N_4 particularly formed 290.48 mmol/g of formate as compared to 259.25 mmol/g by the pristine BiOCl.

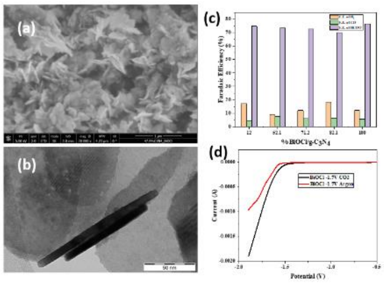

Figure 1*: a) SEM image of 52.1% BiOCl/g-C_3N_4 (b) TEM image of BiOCl showing nanoplate formation (c) F.E. of various %'s of composites (d) LSV graph of BiOCl in Ar and CO_2 atmosphere at -1.7V vs SCE.*

Acknowledgements**:** *This work has been supported by Universities of Trieste and Cádiz and by the Italian Ministry of Education, Universities, and Research (MIUR) through the program PRIN 2017- Project no. 2017PBXPN4.*

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OC23A

THE CHEMISTRY OF Ni-CONTAINING INTERMETALLIC CATALYSTS FOR THE CO_2 HYDROGENATION

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Intermetallics are a large family of inorganic compounds widely studied and applied for their physical and mechanical properties, such as superconductivity and superelasticity. However, their chemical properties were frequently overlooked due to both the inability to predict their formation and apply valence counting rules. In the last decade, the development of new DFT-based bonding analysis tools enabled the study of their chemistry, leading to the successful testing of some representatives as heterogeneous catalysts[1,2].
In this work, $LaNi_5$ and $CeNi_5$intermetallics were investigated as Sabatier catalysts in the 523-773 K temperature range. The best performances were detected for the Ce-containing sample at 723K, with a CO_2 conversion of 63%, and 78% of CH_4 selectivity. XRPD and FESEM analyses revealed that$LaNi_5$ and $CeNi_5$ decompose into metallic Ni and La_2O_3/CeO_2 at the end of catalytic tests. Interestingly, this process was found to start even during the pre-reduction treatment under H_2 flow.
To shed light on this, the chemical bonding of both compounds was investigated by means of cutting-edge position-space techniques, displaying a complex scenario of multi- and 2-atomic Ni–La/Ce polar covalent interactions (Figure 1).

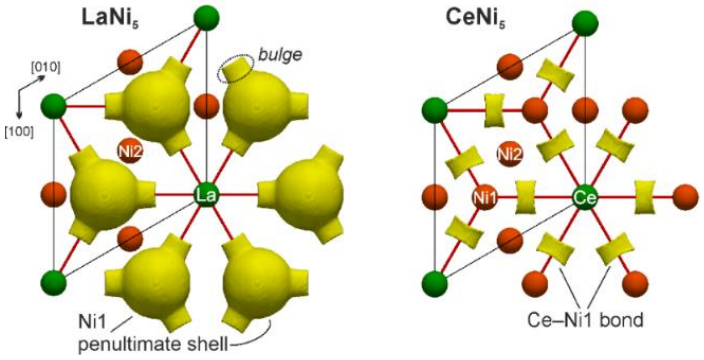

***Figure**: Ni–La and Ni–Ce bonding interactions in the (001) planes, indicated by ELI-Disosurfaces.*

The bonding results enabled a surface simulation, revealing that while H_2 molecules dissociate as hydrides that diffuse into the bulk, Ni atoms migrate toward the surface, well in line with experimental results.

Acknowledgements*: *RF acknowledges University of Genova for funding the project«COMET – CO_2METhanation through interMETallics», Curiosity Driven 2021, funded by the European Union – NextGenerationEU.GG and ES acknowledge National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministerodell'Università e dellaRicerca (MUR); funded by the European Union – NextGenerationEU.

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OC24A

A MORE SUSTAINABLE CATALYST FOR A CIRCULAR HYDROGEN PRODUCTION

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The paradigms of circular economy include for sure the production of sustainable energy but also the valorization of materials that are currently solely seen as waste. Nowadays, sewage sludge (SS) is one of the most abundant waste produced by municipalities and industries, but it can also be a source of valuable chemicals, including some interesting energy vectors[1]. The significant concentration of ammonia in SS[2] is appealing for this purpose: its oxidation does not produce any carbon containing species and it has much lower energy demand compared to hydroxyl oxidation in water splitting[3]. In this work, we investigated a composite system based on metal nanostructures grown on nickel foam (NF) for the electrochemical ammonia oxidation reaction (AOR). NF was selected as a support due to its good electrochemical properties, mechanical stability and high specific surface area. Both platinum and more earth-abundant materials based on Ni and Cu were deposited on NFs by different synthetic approaches in solution (*e.g.*, galvanic displacement, pulsed electrodeposition and hydrothermal method) that allow the growth of high dispersed nanostructures They were characterized and studied for their morphological, crystallographic and electrochemical aspects. Moreover, electrolytic experiments were performed to investigate and compare the stability and selectivity for AOR. Our results showed that Pt has some evident tendency to poisoning while materials based on less noble metals such as Ni and Cu showed longer stability.

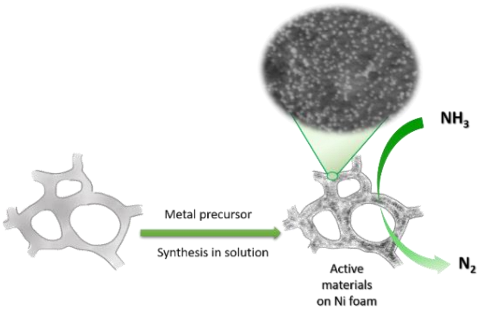

Figure 1: *Preparation of composed nanostructured materials active for the electrooxidation of ammonia*

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OC25A

CHEMICAL BATH DEPOSITED ZN$_{(1-X)}$MG$_X$O BUFFER LAYER FOR CU(IN,GA)SE$_2$ SOLAR CELL

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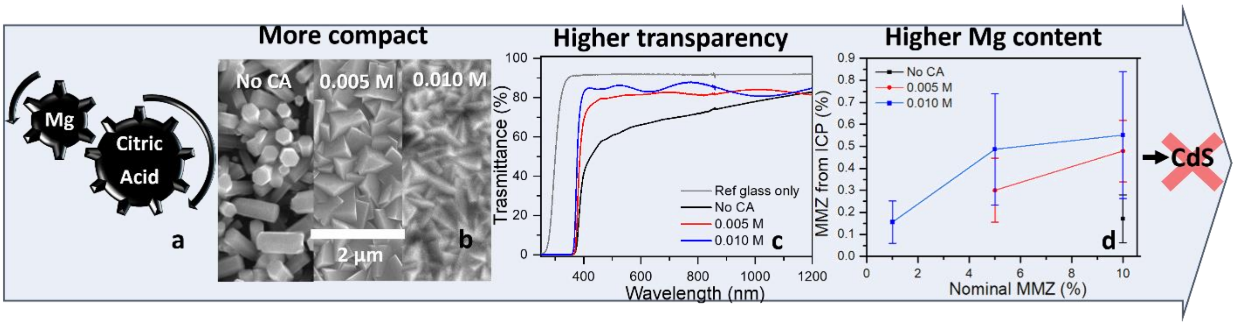

Figure 1*: Tuning citric acid and Mg amounts (a) a more compact film (b) with enhanced transparency (c) and slightly higher Mg content (d) was prepared in view of replace CdS toxic buffer layer. Preliminary results.*

Cu(In,Ga)Se$_2$ photovoltaics (PV) has recently reached an impressive efficiency as high as 23% confirming its central role in PV development.[1] However, the involvement of a toxic CdS buffer layer hinders its commercialization. Several alternative buffers have been studied in the literature with manyphysical or chemical techniques. Interestingly, chemical bath deposition is known to give among the highest efficiency solar cells. (Zn,Mg)O is one of the most promising candidate materials[1]. Nevertheless, when prepared trough chemical bath deposition, the amount of Mg that can be incorporated into the layer is hardly controllable,and it is very low except for a few reports.[2]–[5] In this work, starting from the ZnO deposition of *Kokotov et al.*[6] and the work of *Garzon et al.*[7], the morphological, optical, structural and compositional properties of (Zn,Mg)Owere investigated. First of all, the effect of Mg concentration in the starting bath was studied showing no deposition when a concentration of Mg equal or higher than 35 % [Mg]/([Mg]+[Zn]) (MMZ) was involved. The as prepared (Zn,Mg)O showed a columnar morphology with voids among columns, hence citric acid was exploited due to its widely known ability to passivate the top surface of the columns.[4]The addition of citric acid not only allowed the preparation of a flatter and more compact layer but also increased slightly theMg incorporation. However, the highest Mg concentration measured is still very low (0.5% MMZ through inductively coupled plasma atomic emission spectroscopy). It is believed that the understanding of the coordination chemistry and of the kinetics at play will be crucial in the control over the Mg content.

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OC26A

Co-SUBSTITUTED GLOBINS AS POSSIBLE ELECTROBIOCATALYSTS FOR GREEN HYDROGEN PRODUCTION

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Green hydrogen is the most promising fuel for the future therefore new and efficient routes for its production are required. Although metalloenzymes hydrogenases are one of Nature's way to hydrogen evolution, their instability in atmospheric oxygen and difficulty of overexpression are severe drawbacks that hinder their large scale use [1, 2]. Oxygen tolerant enzymes able to catalyze hydrogen production and displaying higher stability and yield of recombinant expression might therefore represent the key to a bio-based route to green hydrogen [2].

In the last ten years, the incorporation of Co(III)/Co(II) ions into oligo- or polypeptide matrices has emerged as a green, promising route to develop hydrogen evolving water soluble bioinorganic catalysts withstanding exposure to air and working at relatively low overpotential with high turnover numbers [1-4].

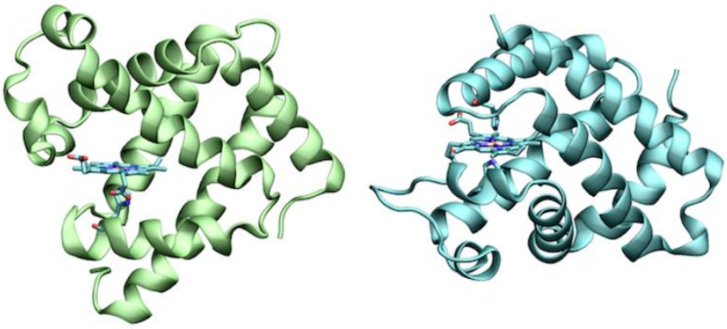

***Figure 1**: Three-dimensional structure of human myoglobin (left) and neuroglobin (right)*

We therefore produced the Co-substituted derivatives of two globins (myoglobin and neuroglobin) and used an electrochemical approach to verify their ability as electrobiocatalysts for the molecular hydrogen evolution reaction from aqueous protons. Indeed, we observed that, upon absorption on the surface of a pyrolytic graphite electrode, both Co-substituted globinscatalyze H^+ reduction in water at relatively low overpotentials, following the Michaelis-Menten model. The catalytic processes is influenced by protein-based acid-base equilibria and by the nature of the Cobalt axial ligands. The data provide some hints about the catalytic mechanism of the electrobiocatalytic production of H_2.

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OC27A

SURFACE FUNCTIONALIZATION AND PHOTOSENSITIZER COUPLING IN HYBRID ZnO/SiO$_2$ NANOSCINTILLATORS

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ZnO is a potential candidate material as scintillator agent for in vivo cancer treatment under X-Rays, due to its ability to adsorb the incoming X-ray beam[1], its photostability and biocompatibility. Its coupling with organic photosensitizers (PS) is crucial to induce the cell cytotoxicity and the production of reactive oxygen species (ROS), stimulated by multiple radiative emission and adsorption processes, as well as suitable energy transfer between ZnO-PS. In this frame, the fine control of the ZnO-PS architecture plays a key role in determining the electronic and luminescent properties of ZnO, and the energy transfer efficiency between the components.

In this work, ZnO-PS structures were designed by using different surface functionalization strategies and their optical properties investigated upon excitation under both ionizing and UV irradiation. The aim is to explore the role of ZnO-PS interaction and their relative distance on the optical behaviour. Thus, ZnO nanoparticles (NPs) were anchored on SiO$_2$ NPs as carrier (ZnO/SiO$_2$) and functionalized with a 5,10,15,20-tetraphenylporphyrin(TPP) used as PS. The coupling was realized by using three different silane-grafting agents through theirhydrolysis and condensation reactions onto ZnO/SiO$_2$ surface. In details, (3-aminopropyl) triethoxysilane (APTES) andp-aminophenyl-trimethoxysilane (PHTMS) were used in combination with a tetrakis(4-carboxyphenyl)porphyrin (TCPP) to promote the interaction between the silane amino groups and the carboxylic functionalities of TCPP[2]. Besides, 3-(trimethoxysilyl)propyl methacrylate (MPTMS) was selected to favour a more stable C-C bond with a methacryl-substituted TPP (MTPP). The structural and surface characterization confirmed the presence of ZnO NPs of 5-6 nm on SiO$_2$NPs (~80 nm). Moreover, Infrared Spectroscopy, Thermogravimetric Analysis and Elemental Analysis validated the successful functionalization procedure of ZnO/SiO$_2$with TPP by using all the silanes, up to 3.0 wt% of TPP over SiO$_2$ surface.

The optical properties were preliminary tested in solid-state and by dispersing the materials in water. Both the Radioluminescence (RL) and the Photoluminescence Analysis (PL) revealed a high luminescence of ZnO NPs; moreover, the TPP emission was strongly enhanced compared to a mechanical mixing between ZnO and TPP, suggesting the occurrence of an energy transfer between the two components, mainly radiative. This depends on the used coupling agents, especially on the distance between ZnO and PS, and was particularly effective in the presence of MPTMS. Moreover, computational simulations on the interaction of hybrid nanosystems with ionizing radiation evidence the key role of the energy deposition within the SiO$_2$ and ZnO components. This mechanism would enable a further sensitization ofporphyrin emission in the hybrid nanosystems. Ongoing tests are necessary to verify the effective production of ROS, especially $^1O_2$ under excitation, to finallypromote their application for in vivo treatments.

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OC28A

PHOTOCHEMICAL IMAGING OF PLASMONIC PHOTOCATALYSTS WITH NANOSCALE RESOLUTION

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Metallic nanostructures support localized surface plasmon resonances that enable light concentration in nanoscale volumes providing enhanced light-matter interactions. These, in turn, can transduce light into chemical energy through various plasmonic effects such as intense near fields, hot carriers, and local heating. The use of plasmonic nanostructures as photocatalysts has become an attractive approach to drive chemical reactions with improved reaction rates and opening to unusual product selectivity by leveraging the induced plasmonic effects. However, mechanistic understanding on how plasmonic photocatalysts activate chemical reaction is still elusive. One approach that can improve our understanding on such complex nanosystems is to map at the nanoscale the material location where the reaction products are generated. In this talk, I will present our recently developed technique that combines several in situ techniques by using scanning photoelectrochemical microscopy and scanning spectrometer microscopy to generate two-dimensional maps of optical properties and photochemical activity of low dimensional photocatalysts (Figure 1). In particular, I will show photochemical activity maps with sub-wavelength resolution of TiO_2 nanotubes functionalized with plasmonic Au NPs showing a bipolar behaviour, thus enabling the detection of both oxidation and reduction products over different locations of the very same nanostructure. These results open the way to quantitative investigations at the nanoscale to evaluate the photocatalytic reactivity of low-dimensional materials in a variety of chemical reactions.

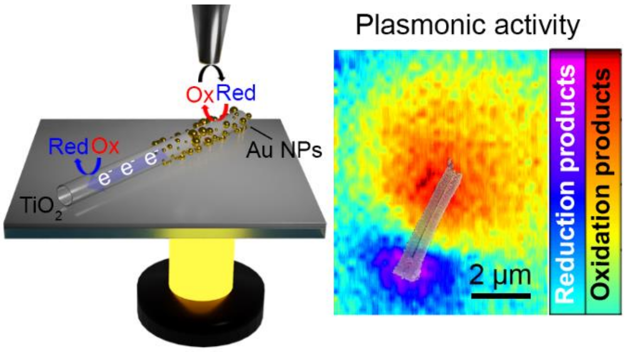

***Figure 1**: Schematic showing (left) the experimental set-up employed for in situ measurements of optical properties and photochemical activity of various plasmonic photocatalysts and (right) a representative two-dimensional activity map of Au/TiO_2 photocatalyst.*

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OC29A

RH AND PD NPS ON WOOL FOR FLOW CONTINUOUS REDUCTIONS

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Heterogeneous catalyst is an attractive form of catalysis, since it guarantees its reuse for several times and it avoids purification steps not causing any leaching in the reaction mixture.[1]

In our work we have found sheep wool as an excellent green support for some metal catalysts; the wool amino-acid structure (with the presence of heteroatoms as N, S, O) allows different attach protocols for many kinds of molecules and metals.[2]

We supported in mild conditions Pd nanoparticles (NPs) and Rh NPs in water and in presence of formic acid; then these catalysts were used to carry out the reduction in batch of maleic acid to succinic acid in water with H_2 or hydrazine sulphate as reducing agent. The reaction in presence of chemical reducing (hydrazine) was reproduced in continuous flow condition: an empty old HPLC column of 10 cm length was filled with the solid catalyst (metal NPs on wool) and the aqueous solution of maleic acid and hydrazine salt was pumped inside it thanks to a syringe pump; pure product solution was collected at the end of column (Fig. 1). The life of packed bed reactor was very long, the yield in succinic acid was 100% at the beginning and then it decreased to 65%. The adopted flow condition set-up allows to recycle catalyst without any step of separation from the reaction mixture (filtration and washing), therefor without lack of catalyst during purification procedure and consequential contamination of working place; another advantage of this method is the increased catalyst stability since it is not stressed by stirrer.[3] On the other hand, the use of wool is an example of valorisation of waste material in order to support the circular economy[4]avoiding environmental pollution and hight costs of disposals.

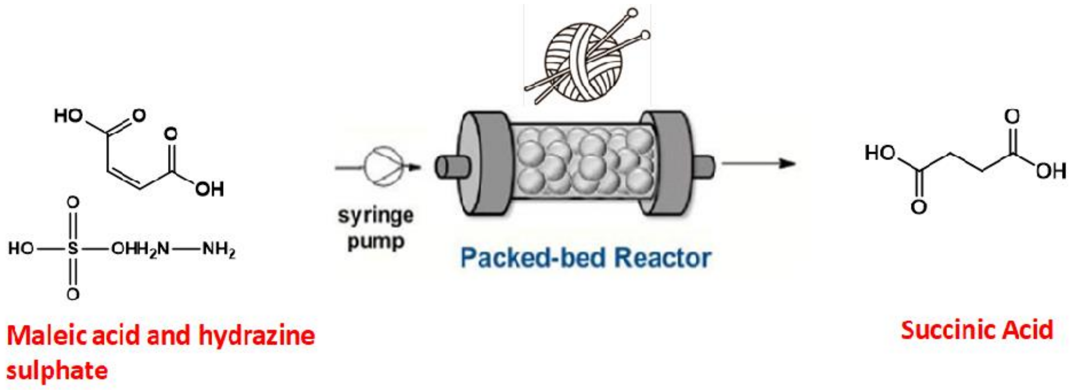

***Fig 1**: reduction of maleic acid to succinic acid by hydrazine sulphate under continuous flow conditions using a packed bed HPLC column as functionalized reactor.*

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OC30A

TUNING THE VISIBLE-LIGHT-DRIVEN PHOTOCATALYTIC PROPERTIES OF MULTI-DECORATED TiO_2 BY NOBLE METALS TOWARDS BOTH PROPIONIC ACID AND NOx DEGRADATION

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Unpleasant odorsare the most disturbing pollutants and the main reason for air quality complaints in urban and industrial areas. Odor emissions consist of various chemical components, some of which can be perceived at very low threshold levels and significantly harm mental and physical health even at very low concentrations.[1]On the other hand, nitrogen oxide (NOx) emissions represent one of the most hazardous air pollutants, causing various environmental and health problems, contributing to ground-level ozone, global warming, acid rain, and urban smog.[2] Moreover, NOx exposure can lead to many respiratory and vision problems, lung dysfunction, and mental diseases.Nowadays, many technologies are available for odors and NOx abatement and control. Among them, photocatalysis carried out under solar or artificial light has been widely applied to address many air, and not only, pollution issues.[3]From the discovery of the water-splitting property of TiO_2 by Fujishima and Honda,[4] its applications in water and air purification under UV irradiation have multiplied due to its extraordinary properties, such as high stability, low cost, high availability, etc. To overcome the limitation of TiO_2 and extend its photo-response to the visible region improving its photocatalytic performance, surface modification with noble metals nanoparticles (NPs) has been studied as an efficient approach.[5]Nevertheless, noble metals' high prices and resource shortage limit their applications. In fact, many studies aim to find alternatives based on cheaper and more abundant materials, such as from noble metals' extraction/processing.[6]

In the present research we report the employ of multiple noble metals-modified micrometric TiO_2-based photocatalysts, prepared by a cheap and sustainable approach based on the use of metal-enriched wastewaters (Ag, Au, Pt) and used for the photodegradation of propionic acid (PA) and NOx under LED irradiation. Properly tuning the metal decoration step, the photoactivityof the materials was optimized. 0.1%Pt@Ag/TiO_2 led to 60% PA removal, whereas thestrong PA adsorption on the 0.1%Au@Ag/TiO_2 surface caused a partial deactivation. In contrast, 0.1%Au@Ag/TiO_2 showed the highest photoactivity in the NOx decomposition(90%) due to thehigh tolerance of Au to HNO_3 produced on the catalyst surface.

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OC31A

ADVANCEMENTS IN PORPHYRIN-SENSITIZED PHOTOELECTROCHEMICAL CELLS FOR TEMPO OXIDATION

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Porphyrin sensitizers play a pivotal role in the development of dye-sensitized photoelectrochemical (DSPEC) devices thanks to their strong UV-Vis absorption, excellent electrochemical and photochemical stability, and adjustable electronic properties through structural modifications.[1] By carefully tuning the porphyrin structure, the ground-state potential of the sensitizers can be optimized to facilitate photo-oxidation processes at the anodic counterpart of DSPEC devices as for hydrobromic acid[2] and water splitting.[3] This crucial attribute can be attained by incorporating electron-withdrawing groups as fluorine atoms into the porphyrin core, inducing a significant electron deficiency. Recently, the implementation of porphyrin sensitizers in the oxidation of the stable organic radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) has gained significant attention.[4]

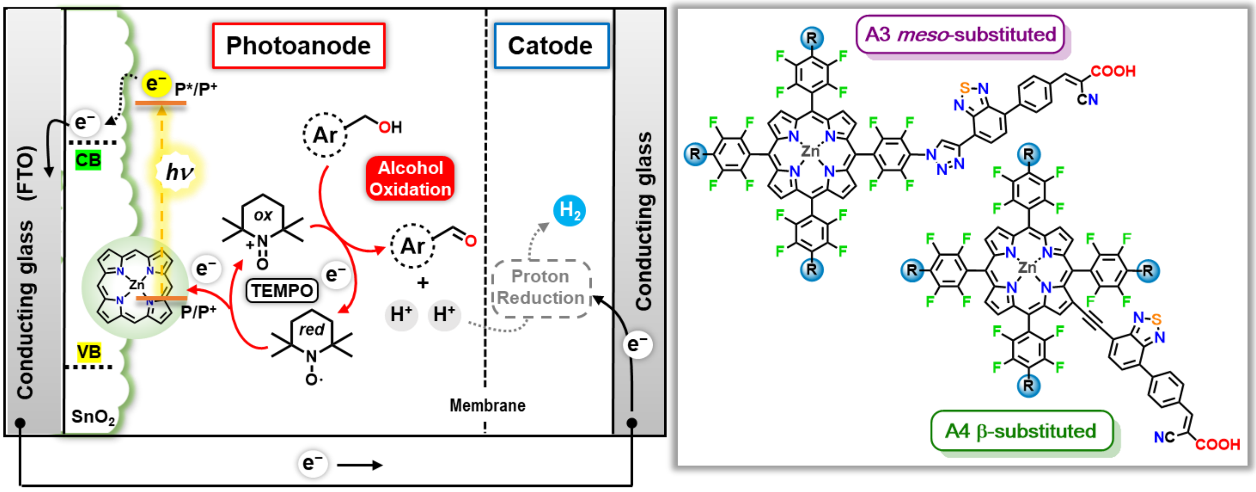

Figure 1: *caption (Times New Roman, 10 pts, centred, Italic)*

In this contribution, we report a novel series of perfluorinated Zn^{II}-porphyrin-based sensitizers specifically tailored for TEMPO oxidation (Figure 1). A4 β-pyrrolic and A3B meso-substituted zinc porphyrins, equipped with both donating amine groups and π-accepting spacers to optimize donor-acceptor interactions, are investigated. The impact of the molecular design of porphyrins on electronic properties is comprehensively explored through a combination of electrochemical, spectroscopic, computational, and photophysical analyses. The key parameters which govern the performances of porphyrin-based DSPEC devices for TEMPO oxidation are also evaluated. The insights gained from these studies pave the way for the development of efficient and stable DSPEC systems for energy conversion and storage applications.

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OC32A

PARAMAGNETIC ^{1}H NMR DOSY SPECTROSCOPY REVEALS THAT DINUCLEAR BIS-β-DIKETONATE COMPLEXES REARRANGE TO MONONUCLEAR IN ORGANIC SOLUTION

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Diffusion Ordered Spectroscopy (DOSY) is a well-known technique to deconvolute complicated ^{1}H NMR spectra of mixtures, while at the same time it allows to estimate the molecular weight (*MW*) of the components. In fact, DOSY spectroscopy measures the diffusion coefficient (*D*) of each species, which is related to its *MW* through the power law $D = K \cdot MW^{\alpha}$; *K* and *α* are empirical parameters from external calibration curves.[1,2] While the determination of *MW* by DOSY is ordinary for small organic molecules and for polymers, successful applications to paramagnetic complexes of transition metal[3] or lanthanide ions[4] are rare. In fact, the large paramagnetic shifts and broadenings of the proton signals make the DOSY analysis extremely challenging.

Despite this, we were able to exploit paramagnetic DOSY spectroscopy to clear up an intriguing structural problem. The bis-β-diketonate complexes [Co(bdhb)py$_2$] and [VO(bdhb)], shown in Fig. 1 (left), were designed as simple mononuclear (MN) metal-organic paramagnets for spintronics applications (H_2bdhb = *m*-bis(3,5-dioxohexyl)benzene; py = pyridine). In addition, a diamagnetic analogue [Zn(bdhb)py] was also prepared for comparison. Surprisingly, all these compounds were found to systematically crystallize in dinuclear (DN) form, namely as [Co$_2$(bdhb)$_2$py$_4$], [(VO)$_2$(bdhb)$_2$], and [Zn$_2$(bdhb)$_2$py$_2$] (Fig. 1, right). However, DFT calculations predict that MN species should be strongly stabilized over DN ones in organic solution. Clearly, MN and DN forms are difficult to distinguish in solution by techniques like FT-IR, UV-Vis-NIR, and ^{1}H NMR spectroscopies, although signals attributable to MN complexes were observed in the ESI-MS spectra. Here, *MW* estimation by ^{1}H NMR DOSY technique brilliantly demonstrated that all three complexes are MN in organic solution. Therefore, DOSY spectroscopy should be regarded as an outstandingly powerful technique in coordination chemistry to characterize the nuclearity and/or the aggregation state of metal-organic compounds, including paramagnetic ones.

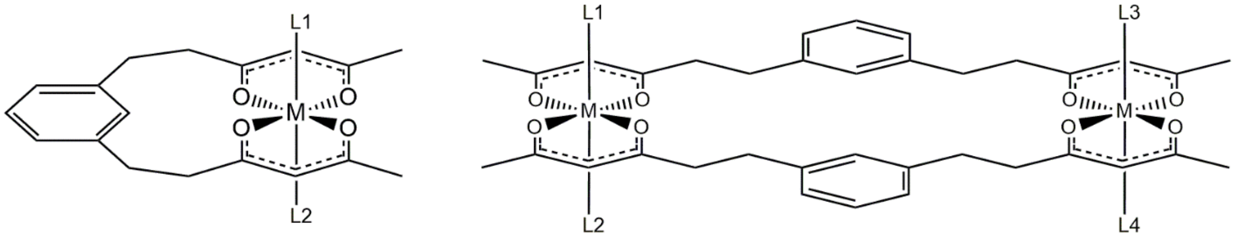

***Figure 1**: Left, mononuclear complexes (for M = Zn^{2+}, L1 = py; for Co^{2+}, L1 = L2 = py; for V^{4+}, L1 = O^{2-}). Right, dinuclear complexes (for M = Zn^{2+}, L1 = L3 = py; for Co^{2+}, L1 = L2 = L3 = L4 = py; for V^{4+}, L1 = L4 = O^{2-}).*

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OC33A

ARTIFICIAL HEME-ENZYMES FOR THE CONSTRUCTION OF FUNCTIONAL NANOMATERIALS

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Recent advances in the field of enzyme design and engineering have significantly expanded the chemist's toolbox, providing a collection of catalysts tailored for specific applications.[1]

In this context, we have developed a class of miniaturized heme-enzymes, named Mimochromes (MCs), inspired by the active site of peroxidases.[2] Owing to their reduced size (~3 kDa), MCs lie at the interface between metalloproteins and small-molecule complexes, combining the exceptional catalytic performances of natural enzymes with the promiscuity of synthetic catalysts. Among them, we have identified MC6*a as the lead compound and demonstrated its ability to host and modulate the reactivity of different metal ions in the frame of oxidation [3-5] and energy-related [6] catalysis.

Within the efforts of exploiting MCs for practical uses in catalysis and sensor technology, we have analysed their behaviour upon immobilization onto different surfaces.[7] Our most recent studies show that FeMC6*a can be efficiently immobilized onto differently shaped gold-based nanomaterials, retaining its structural and catalytic properties. With the aim of developing innovative, sustainable and cost-effective functional nanomaterials, we are currently assembling completely peptide-based nanostructures. To this end, we have selected and modified amyloid forming peptide sequences to achieve functionalized fibrils displaying our miniaturized heme-enzymes. Structural and catalytic studies demonstrate the feasibility of this approach, opening the chance to a plethora of applications in the field of biosensing and catalysis.

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OC34A

LANTHANIDE METALLO-LIGANDS FOR THE SYNTHESIS OF HETERONUCLEAR Pt_2Eu_2 LUMINESCENT ARRAYS

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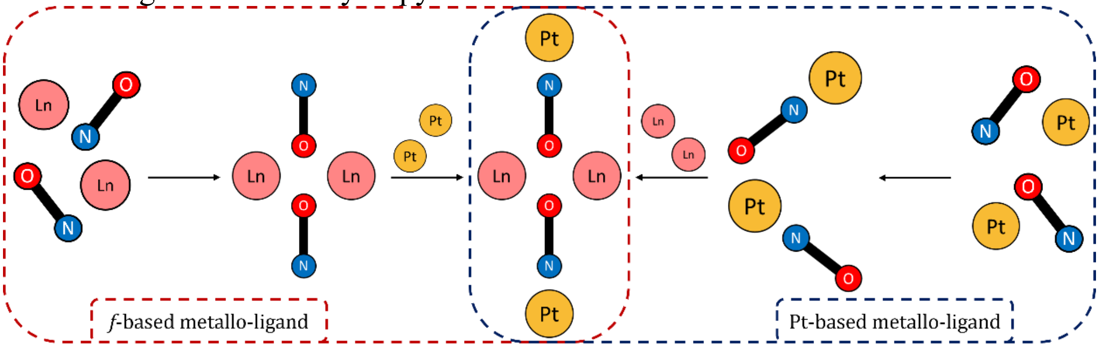
In the last decades rare-earth complexes have been highly studied due to their luminescent properties, exploitable in many different fields.[1] Many research efforts have been devoted to the design of innovative lanthanide-based luminescent thermometers.[2],[3]A family of homodinuclear Ln^{3+} (Ln: Gd, Eu) luminescent complexes with general formula $[Ln(\beta\text{-diketonato})_3(\mu\text{-}N\text{-oxide})]_2$ has been recently developed to study the effect of the β-diketonato and *N*-oxide ligands on their thermometric properties.[3] We report here that $[Ln(tta)_3(\mu\text{-pyrzNO})]_2$,[3] (Ln: Eu, Gd,Htta: thenoyltrifluoroacetone,pyrzNO: pyrazine *N*-oxide) presenting a pending nitrogen donor functionality, can behave as a ligand for an open site platinum coordination sphere in the reaction with $[Pt(\mu\text{-}Cl)Cl(EPh_3)]_2$ (E: P, As). New heterometallic complexes with formula $[Ln(tta)_3(\mu\text{-pyrzNOPtCl}_2EPh_3)]_2$ (Ln: Eu, Gd; E: P, As) have been isolated and crystallographically characterized. The dinuclear lanthanide unit $[Ln(tta)_3(\mu\text{-pyrzNO})]_2$ is sufficiently inert to be used as a *f-based metallo-ligand* but it is also sufficiently stable to be formed in mild conditions starting from a *d-based metallo-ligand* [PtCl(ppy)pyrzNO] (Hppy: 2-phenylpyridine) with a pending oxygen donor functionality and the $[Ln(tta)_3]$ fragment (**Scheme 1**). Also the heterometallic complexes $[Ln(tta)_3(\mu\text{-pyrzNOPtCl(ppy)})]_2$ (Ln: Eu, Gd)present a dinuclear lanthanide core bridged by two oxygen atoms. In all molecular complexes, platinum is bonded to the nitrogen functionality of pyrzNO.



Scheme 1*: The two synthetic pathways for the synthesis of the Ln/Pt heterometallic arrays*

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OC35A

INVESTIGATING THE REACTION MECHANISM AT THE MICROSCOPIC LEVEL: CROSSED MOLECULAR BEAM STUDIES OF THE REACTIONS BETWEEN ATOMIC OXYGEN AND SMALL AROMATIC COMPOUNDS

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Given the significance of aromatic compounds in various fields such as atmospheric pollution, combustion chemistry, and astrochemistry, we have initiated a systematic laboratory investigation of the reaction mechanism at the microscopic level for their reactions with atomic oxygen. Specifically, we have focused on benzene, pyridine, toluene, and thiophene, as these compounds are commonly found in the aforementioned environments and can serve as simple prototypes for the reactions involving polycyclic aromatic hydrocarbons (PAHs), nitrogen-containing polycyclic aromatic hydrocarbons (PANHs), and polycyclic aromatic sulfur heterocycles (PASHs).

In our laboratory, we use the crossed-molecular-beam (CMB) technique with mass-spectrometric detection (empowered by soft-ionization) and time-of-flight analysis to tackle the reaction mechanism and determine the branching fractions (BFs) [1]. To support the interpretation of our experimental findings, we performed high-level ab initio electronic structure calculations of potential energy surfaces (PESs) and utilized RRKM/Master Equation computations to determine the product BFs[2-4].In the reactions involving O(^{3}P) and benzene or pyridine, we have observed products originating either from one or more H-displacement channels or from a ring-contraction mechanisms which leads to the formation of carbon monoxide (CO). In particular, the presence of a nitrogen atom in the aromatic ring increases the likelihood of the ring-contraction mechanism that accounts for 98% of the reaction O + pyridine, while in the case of the reaction with benzene it accounts for *ca*. 30% under the same experimental conditions[2-4]. This can be rationalized by considering the occurrence of intersystem crossing (to the underlying singlet PES) in the entrance channel for the *ipso*- approach in the case of pyridine which becomes, somewhat unexpectedly, the most effective attack site.[4] Conversely, in the case of toluene, the presence of a methyl group seems to help in preserving the six-membered aromatic ring possibly because of an easy CH_3/O exchange channel[5]. The reaction with tiophene will illustrate further the role of presences of heteroatoms in the aromatic ring.

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OC1B

A NOVEL RU(II)-BASED COMPOUND ACTIVE IN PACT CANCER THERAPY: THEORETICAL STUDY OF THE MECHANISM OF ACTION AND OF THE PHOTOPHYSICAL PROPERTIES.

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Phototherapy, in particular the young treatment of photoactivated chemotherapy (PACT), has gained extensive attention in cancer therapy owing to its minimal invasiveness and high spatial and temporal controllability. PACT agents can act with novel or poorly understood mechanisms of action. In particular, upon irradiation, the photoactivatable agent undergoes a series of transformation which generate the formation of the active species capable of carrying out the cytotoxic action. Currently, several types of coordination complexes containing Pt(IV),[1]and Ir(III)[3] together with Rh(III)[4] and Ru(II)[5] are under investigation for their application in PACT.Among theme, Ru(II)-centered complexes and, in particular, polypyridyl ruthenium compoundsare emerging as effective agents. It was shown that these complexes can undergo ligand dissociation after photo-irradiation and the resultant "uncaged" metal compounds, the Ru(II) aqua complexes, can bind to DNA in a manner similar to cisplatin and induce cell death. [6]Here, the outcomes of a thorough density functional theory (DFT) investigation, performed adopting a new computational work-flow set up for the study of the photoinduced activation mechanism in PACT therapy,arereported.All the photophysical propertiesof a recently synthetized Ru complex,[7] $[Ru(dpp)(bpy)(mtmp)]^{2+}$ (Fig. 1) have been explored and the photodissociation mechanism has been elucidated in detail.

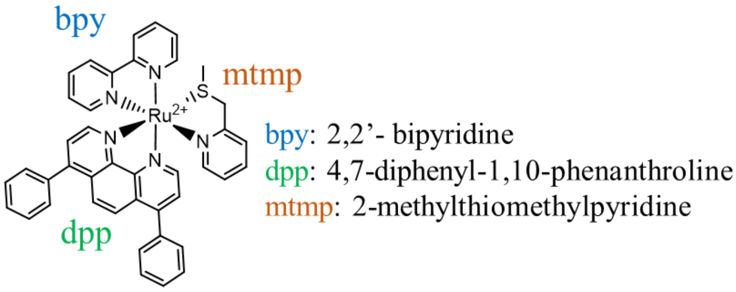

Figure 1. *Schematic representation of the Ru complex under investigation.*

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OC2B

EFFECTIVE CONTROL OF CRYSTALLIZATION OF INORGANIC SYSTEMS BY SPATIAL CONFINEMENT

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In recent years, nanoscale confined spaces have been successfully employed as fascinating environments for the spatially and phase-controlled synthesis of inorganic systems, possibly enabling aprecise control on the reaction pathway as well. Indeed, it has been reported that space constraint affects the physical properties of molecules (*e.g.* dielectric constant, phase behaviour and anisotropic orientational dynamics of water dipoles), as well as the subsequent chemical transformations occurring within these enclosed volumes,[1,2] albeit its role in determining the synthetic outcome is currently not fully understood.
Herein, we address case studies dealing with the investigation of differently sized enclosed environments as reactors for the spatially controlled synthesis of model inorganic systems, systematically evaluating the effect of space confinement on the synthesis outcomes. In particular, different classes of inorganic materials, encompassing metal oxides, metal sulfides and metal nanoparticles, were synthesized in the increasingly constrained environment represented by i) a continuous flow microreactor (10 µm-1 mm), ii) nanodroplets produced by inverse miniemulsions[3] (50-300nm) and iii) nanopores of mesoporous materials(2-50nm).To track and understand the impact of the space confinement, the systematic and comprehensive experimental approach was supported by a wide array of characterization techniques, carrying out a careful structural and morphological investigation both by *ex situ* standard (XRD, TEM, SEM) and by advanced *in situ* time-resolved techniques (SAXS/WAXS and XAS) performed at synchrotron facilities.

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OC3B

SYNTHESIS OF SUB-100nm CARBON NANOPARTICLES WITH A FINE-TUNING OF THE SIZE, ANTIOXIDANT AND PHOTOTHERMAL PROPERTIES

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Hydrothermal carbonization (HTC) of carbohydrates has been reported as a sustainable and green technique to produce novel carbonaceous micro and nanomaterials, with a minimum reported size of 100 nm, excluding sub-10 nm nitrogen doped carbon dots. These materials have been developed for several applications, including catalysis, separation science, metal ion adsorption, medicine and so forth [1]. Lately, has been reported that carbon nanoparticles (CNP), obtained through the HTC of glucose, possess interesting photothermal properties when irradiated by near-infrared (NIR) light, act as antioxidant by scavenging reactive oxygen species (ROS), and present good biocompatibility [2]. Decreasing and fine-tuning the size of CNP is crucial to exploit these materials especially in bio-medical applications, along with the understanding and the control of the mechanism behind their properties. In this work, a new HTC synthesis method to obtain glucose derived CNP in the 15-150 nm size range with a precise control of the diameter is presented, together with an advance in the understanding of the reaction mechanism behind HTC. Moreover, modifications of the synthetic strategy and a post-synthesis process were applied to increase the graphitic degree of CNP, resulting in an increase of the photothermal and ROS scavenging activities, without affecting morphological and colloidal properties of the material.

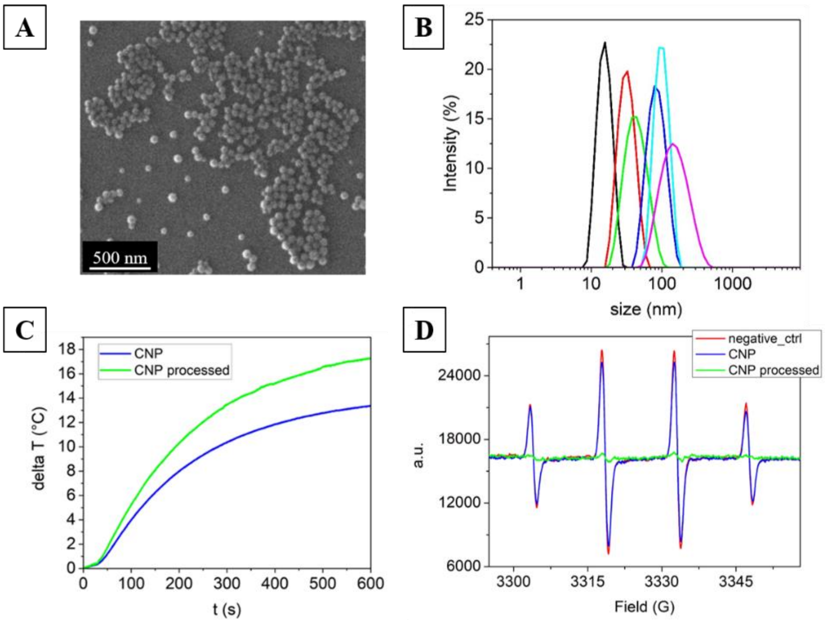

Figure 1: *(A) FESEM image of CNP; (B) CNP size tuning: size distribution by DLS; (C) photothermal activities of CNP; (D) ROS scavenging ability of CNP measured by EPR*

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OC4B

DESIGN AND DEVELOPMENT OF SUSTAINABLE NANOTECHNOLOGICAL PROTECTIVE HYBRID MATERIALS IN SURFACE PROTECTION TREATMENT

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Hybrid organic-inorganic nanomaterials, featuring functional nanomaterials (nanofillers) in combination with organic/inorganic polymeric matrices (either based on sol-gel or synthetic/natural organic polymers), currently find useful applications in many industrial sectors. The main reason stands in the possibility that these innovative materials offer of being chemically/physically modified at a nano dimensional level and suitably functionalized for the treatment of different kind of surfaces to give them final implemented chemical, physical and mechanical properties. In particular, in protection surface treatments field, the simplest, most efficient and versatile methodology to modify the surface of different materials, with a view to moving towards increasingly sustainable and eco-friendly materials, also improving their properties, involves the use of sol-gel eco-friendly based materials to be used as coating systems. Recent literature highlights the characteristic properties of nanomaterials and their possible use in the development of widely employed hybrid sol-gel matrices for the development of useful coatings for corrosion mitigation on different metallic surfaces, as well as hydrophobic and antifouling coatings for different application fields like blue-growth, buildings, cultural heritage and textiles sector.

The main goal of the present study was to investigate and evaluate many types of sol-gel based coatings that may be applied to various substrates in order to change and improve their surface characteristics. In particular, this work was aimed to the development of three different type of nanostructured hybrid coatings and surface finishing for anticorrosive, hydro-repellent and antifouling applications and the related properties; their most important applications were described, also addressing the actual need to design and produce new materials with a lower impact on the environment.

The first challenge refers to the development and study of chromium-free nanotechnological primer systems capable of effectively and durably preventing the corrosion of surfaces in the aqueous phase.[1] The second challenge concerns the design and development of eco-friendly and innovative fouling release coatings to overcome the biofouling issue.[2] Finally, the third one focuses on the preparation of sol-gel based coatings for textile fabrics, and evaluation of their hydrophobic properties.[3,4]

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OC5B

DIIMINE-DITHIOLATE PLATINUM COMPLEXES FOR ICT APPLICATIONS: CASE STUDIES ON THIRD-ORDER NONLINEAR OPTICAL PROPERTIES AND PHOTOCONDUCTIVITY

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The past thirty years have witnessed a great deal of interest in platinum diimine-dithiolate complexes [Pt(N^N)(S^S)] due to properties including solution luminescenceandsolvatochromism.[1]Their second-order nonlinear optical (NLO) properties were also studied prompted by their lack of an inversion centre, while third-order NLO properties have been only occasionally tapped. Moreover, besides their use as active layers in dye-sensitized solar cells, the applications of these systems in optoelectronics have scarcely been investigated.

We report here on the synthesis, characterization, and testing of diimine-dithiolate Pt(II)complexes as materials for Information and Communication Technology (ICT) applications.In particular, the third-order NLO properties of a series of [Pt(N^N)(S^S)] complexes featuring 5,6-dihydro-1,4-dithiin-2,3-dithiolate (dddt^{2-}) or 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate (pddt^{2-}) as S^S ligands, along with 1,10-phenanthroline (phen) or 2,2'-bipiridine (bipy) derivatives were investigated.[2] In addition, a case study on the photoconductive properties of [Pt(bipy)(Naph-edt)] (bipy = 2,2'-bipyridine; Naph-edt^{2-} = 2-naphthylethylene-1,2-dithiolate)is reported (Figure 1).[3]

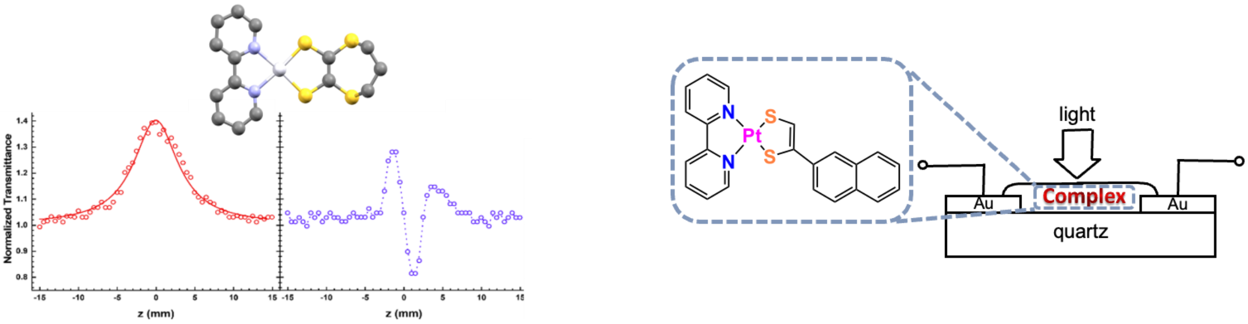

Figure 1: *Molecular structure of [Pt(bipy)(pddt)] along with itsopen-apertureand divided Z-scans (left); schematic representation of the device employed to study the photoconductivity properties of [Pt(bipy)(Naph-edt)] (right).*

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OC6B

DESIGNING GOLD-BASED NANOMATERIALS FOR OPTOELECTRONICS: THE ROLE OF SURFACE LIGANDS

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Gold nanoparticles (AuNPs) represent fascinating nanomaterials showing unique chemical, electrical, and physical properties due to quantum effects. Key properties of nanoparticles can be tailored by altering their physical geometries or modulating the surface stabilizing agent.[1,2] Spherical AuNPs offer resonance wavelengths in the visible region (as the Localized Surface Plasmon Resonance phenomenon, LSPR) that strongly depend on the size, shape, surface, and agglomeration state[1]. The LSPR phenomenon coupled with advances in nanomaterial syntheses, surface stabilization, and self-assembly, has improved the use of gold nanostructures for optical, electrical, and optoelectronics applications. Recently, we explored the functionalization of AuNPs with different surface ligands: mono- and bifunctional thiol-based molecules bearing conjugated organic or organometallic moieties.[3-6] Specifically, two categories of functionalized agents were explored: (i) aromatic thiols containing fluorenyl spacer and fluorescent anthracenyl moiety; (ii) rod-like bifunctional organometallic thiols containing square-planar Pt(II) centers. The presence of a bifunctional rigid spacer with an extended π-conjugated electronic system allowed for the synthesis of covalently linked AuNPs with regularly spaced interparticle distances. AuNPs growth was obtained by a two-phase wet chemical reduction method starting from Au^{3+} containing precursor under inert conditions at room temperature, using $NaBH_4$ as the reducing agent. Size, shape, optical properties, and crystalline structure of these functionalized nanoparticles were determined by solid-state microscopies (FESEM-EDS, AFM, TEM), and spectroscopic techniques, *i.e.*, UV-Vis, infrared spectroscopy (Mid-IR and Far-IR region), ^{1}H and ^{31}P nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy (XPS). In colloidal suspension, the hydrodynamic diameter value ($<2R_H>$) was evaluated by dynamic light scattering (DLS). To extend the versatility of these systems, blends of AuNPs with different π-conjugated polymers, *e.g.*, poly(3-hexylthiophene) (P3HT) and poly(phenylacetylene) (PPA), were prepared. Electric response of pristine functionalized AuNPs and nanocomposite systems were assessed via I/V measurements onto spin coated electrodes.

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OC7B

INTERFACE DIFFUSION AND COMPATIBILITY OF PEROVSKITE ELECTRODES IN CONTACT WITH SOFC/SOEC ELECTROLYTES

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$Ba_{1-x}La_xFeO_{3-\delta}$ perovskites (BLF) transporting electrons, protons, and oxygen ions, are promising oxygen electrodes for solid-oxide cells (SOFC fuell cells or SOEC electrolyzers) in prospected large-scale power-to-gas energy storage systems. [1]
We annealed BLF with 5-50% lanthanum at high temperature in contact with oxide-ion conducting $Ce_{0.8}Gd_{0.2}O_{2-x}$ and proton-conducting $BaZr_{0.825}Y_{0.175}O_{3-x}$ electrolytes, to reproduce thermal aging due to prolonged operation. Employing both bulk X-ray diffraction on powders and synchrotron X-ray microspectroscopy on ceramic bilayers, we followed the solid-state chemical interaction between electrode and electrolyte materials at the micrometer scale, in terms of cation interdiffusion, exsolution and formation of secondary phases.
We find that the Goldschmidt tolerance factor, in turn determined by the La/Ba ratio, drives the stability of BLF perovskite phase in contact with other phases: in this respect, doping the B-site with large cations (Zn^{2+}, Y^{3+}) may increase structural stability. Although extensive reactivity and cation interdiffusion are often observed, we put forward that the products of such interfacial reactions, e.g. $Ba(Ce,Gd)O_{3-x}$ and $(Ba,La)(Fe,Zr,Y)O_{3-\delta}$ among others, may possess some ion-conducting or mixed-conducting qualities themselves, and not necessarily hamper the cell operation. [2]
This complements earlier XANES, EXAFS and X-ray Raman scattering results [3,4] in a complete picture of the defect chemistry of BLF as an oxygen electrode for solid-oxide cells.

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OC8B

ATOMISTIC MODELING OF CHIRAL LEAD- AND TIN- PEROVSKITES

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Hybrid organic–inorganic perovskites have emerged as excellent materials for solar cell applications. Indeed, their extreme tunability and facile synthesis have opened the door to many new applications. Chiral hybrid perovskites are attracting great interest as promising chiroptoelectronic systems with potential for employment in optoelectronics, spintronics, and other applications. To date, the mechanism through which a chiral bias is generated from a chiral organic ligand to an inorganic lattice has remained unclear. In this study,[1] we present a bespoke simulation workflow based on DFT and TD-DFT for studying the chiroptical response of lead- and tin-based 2D chiral perovskites, namely 2D R- and S-$(MBA^+)_2PbI_4$[2] and R- and S-$(MBA^+)_2SnI_4$[3]. The most impacting factors influencing their CD signals were explored through ab-initio molecular dynamics simulations and the analysis of the density of electronic states (DOSs) showing that the relevant chiroptical features are associated with a chirality transfer event driven by a metal–ligand overlap of electronic levels. This effect is more evident for tin-based chiral perovskites showing higher chirality with excitonic coupling, starting from the chiral ligands propagating within the inorganic layer. The difference between tin and lead is due to the higher mixing of metal–ligand electronic states of the tin chiral perovskite, inducing chiroptical signals with wavelengths in the range of 350–500 nm. These signals are red-shifted within the range of 500–600 nm for the lead chiral perovskite. The high electronic coupling between the chiral ligands and the tin octahedra can be ascribed to the radically different assembling of the chiral ligands encapsulated in the tin perovskite, resulting in a highly distorted coordination forming CH–p interactions with a distance value of 3.2 Å, not formed in a lead-based system.

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OC9B

ROLE OF TRANSITION METAL COMPLEXES IN MODULATING AMYLOID AGGREGATION IN NEURODEGENERATIVE DISEASES

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Recently, metallodrugs gained considerable attention in the field of neurological disorders since they show promising in modulating amyloid aggregation, which is a hallmark feature of several neurodegenerative diseases [1]. These diseases are characterized by the accumulation of misfolded proteins, such as amyloid-beta (Aβ) in Alzheimer's disease and alpha-synuclein in Parkinson's disease, and the subsequent formation of amyloid plaques [2]. Transition metal complexes, thanks to their unique characteristics, are able to interact with amyloid proteins through the coordination, oxidation or hydrolysis mechanisms and to inhibit or enhance the formation of large oligomers (Figure 1). Herein, we report on the ability of several metal complexes to modulate the amyloid aggregation of model amyloid systems, in detail, several Pt- [3], Mn-, Re-based complexes with carbon monoxide releasable molecules (CORMs) [4]. By means of different spectroscopic (e.g., fluorescence assays, UV-vis absorption, and electrospray ionization mass spectrometry) and microscopic (scanning electron microscopy and confocal microscopy) techniques and cellular assays, their Mechanisms Of Action (MOAs) have been elucidated. Overall data can open new perspectives for the application of metal-based agents as potential new therapeutic drugs in neurodegeneration.

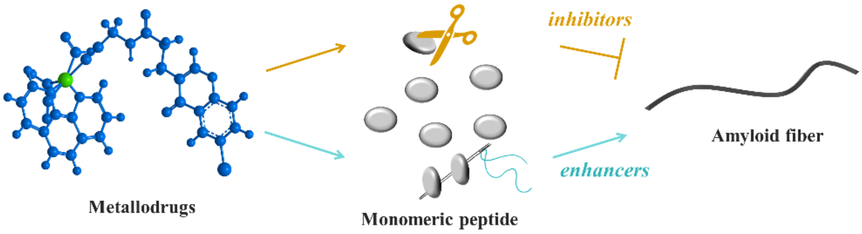

Figure 1: *Schematic representation of MOAs of metallodrugs toward amyloid model peptide*

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OC10B

THE ABILITY OF LYCORINE TO INTERERE WITH COPPER(II) – AMYLOID β ASSOCIATIONS

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Lycorine (LYC) is a very interesting molecule exhibiting a broad spectrum of biological functions [1], including antibacterial[2], anti-inflammatory[3], antitumor[4], and AChE inhibitory activity[5]. Furthermore, a recent study corroborates LYC ability to suppress stress-induced premature cellular senescence by stabilizing the genome of human cells, potentially delaying the onset of age-associated diseases like Alzheimer Disease (AD)[6]. AD is a very debilitating disease with no available cure so far. AD has a multifactorial aetiology leading to inexorable symptoms like brain shrinkage, memory loss and motor dysfunction. The main AD features are (i) amyloid deposition in the brain, (ii) high levels of oxidative stress, (iii) abnormal metal homeostasis and (iv) impaired mitochondrial functions[7]. Recently we have demonstrated that LYC weakly interact with the monomeric Aβ peptide as proved by NMR and CD analysis[8]. Our findings indicate that the alkaloid regions exhibiting the largest effects upon Aβ addition is the pyrrole portion pointing out that the Aβ40-alkaloid association is mediated by the tertiary amino group, positively charged at the applied experimental conditions. At the same time, LYC induces slight changes on the N-terminal residues (His, Asp, Glu) of Aβ strongly suggesting the involvement of this region in the alkaloid interaction. In addition, our data point out LYC performance in reducing ascorbate oxidation, supporting its ability to effectively prevent ROS production induced by copper(II)[8]. In order to better understand the role played by LYC, we have recently investigated LYC- Aβ16 association to clarify Aβ residues involved in LYC binding and to evaluate the effect of LYC in Cu(II) - Aβ16 interaction, which also occurs at the N-terminal region[9].

Acknowledgements: *The authors thanks the Italian MIUR, through the PRIN (Programmi di Ricerca di Rilevante Interesse Nazionale) and the ConsorzioInteruniversitarioRisonanzeMagnetiche di Metallo Proteine (CIRMMP).*

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OC11B

WIREFRAME DNA ORIGAMI AS POTENTIAL CARRIERS FOR PLATINUM COMPOUND IN CANCER THERAPY

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The field of nanotechnology has witnessed a revolutionary advancement with the introduction of DNA origami in 2006.[1] These nanoscale structures, characterized by their precise shape and size, controllability, biocompatibility, and capacity to transport pharmaceuticals or biomolecules, hold great promise as vehicles for therapeutic delivery. Various techniques have been developed to manipulate and fold DNA origami, resulting in compact lattice-based designs as well as more deformable wireframe structures. The latter exhibit enhanced stability, making them particularly suitable for applications in physiological buffers. [2] Driven by the anticancer and antiviral properties of the FDA-approved cisplatin, there has been a surge in interest surrounding platinum-based complexes, leading to the synthesis of numerous new compounds. [3] Among these, phenanthriplatin has shown remarkable antitumor activity surpassing that of cisplatin, owing to its ability to bind to DNA at a single site and inhibit transcription. [4] This study focuses on investigating two different wireframe DNA origami nanostructures, namely the Hexagonal Rod and the Ball (Figure 1), as potential carriers for platinum compounds in cancer therapy. Specifically, cisplatin and phenanthriplatin were employed as model compounds to evaluate the loading capacity, stability, and modulation of cytotoxicity of the nanostructures in immortalized cancer cell lines (A549, HeLa, MCF-7). The results reveal that nanomolar quantities of the Ball-like DNA origami nanostructure, loaded with phenanthriplatin, reduces cell viability in MCF-7 to 33%. However, the loaded structures exhibit no significant effect on the other examined tumor cell lines. These findings offer valuable insights into the utilization of wireframe DNA origami as a promising platform for targeted delivery of platinum compounds in cancer treatment, potentially overcoming platinum resistance.

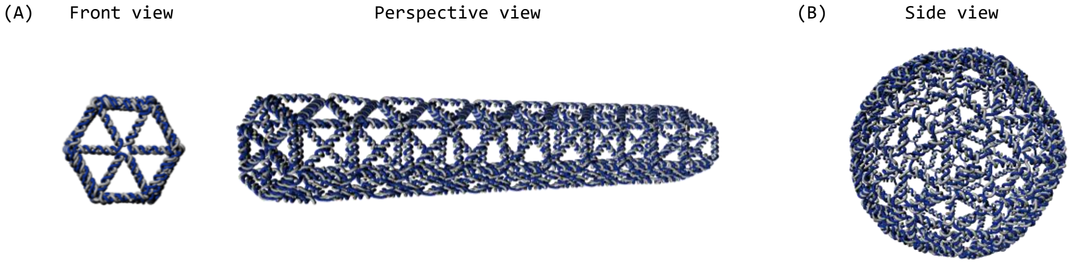

***Figure 1**: Rendering of the investigated DNA origami nanostructures. A) Hexagonal Rod, B) The Ball.*

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OC12B

PEPTIDE-BASED SUPRAMOLECULAR CONTRAST AGENTS FOR MRI APPLICATIONS

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The use of Gd (III) complexes as T_1 Magnetic Resonance Imaging (MRI) contrast agents (CAs) has been questioned because of the evidence of ions accumulation in body districts of patients receiving multiple doses.[1] For this reason, Peptide-Based Hydrogels and Nanogels (PBHs and PBNs) have been proposed as supramolecular systems to encapsulate Gd (III) complexes in order to protect them from transmetallation phenomena occurring *in vivo* and being responsible of Gd (III) release.[2] Moreover, the generation of supramolecular CAs can allow to increase the efficiency of the contrast, in terms of relaxivity value. This strategy has been exploited also to improve the relaxation behavior of highly stable Fe (III) complexes, recently emerged as valuable alternatives to the classical Gd (III) ones, basing on the expectations that the employment of an essential metal ion avoids the occurrence of toxic effects.[3] Here we describe the synthesis, and the formulation of some examples of peptide based HGs and NGs encapsulating iron complexes as supramolecular CAs. The in vitro structural and relaxometricbehavior has been also reported.

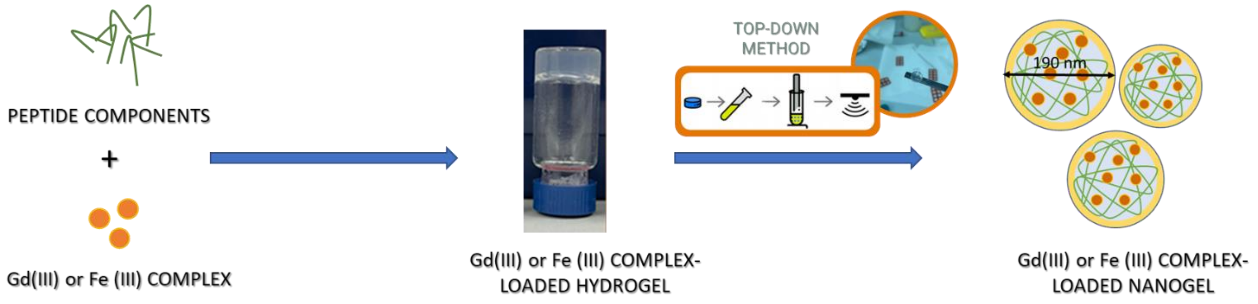

***Figure 1**: Schematic representation of components and methods used to obtain the supramolecular contrast agents.*

***Acknowledgements**: PRIN 2017A2KEPL project "Rationally designed nanogels embedding paramagnetic ions as MRI probes"*

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OC13B

WATER-SOLUBLE RU(II) COMPLEXES AND RU-MICELLES AS EFFICIENT CATALYSTS FOR TRANSFER HYDROGENATION REACTIONS INVOLVING BIOMOLECULES

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Metal-based compounds known as transfer hydrogenation catalysts have shown to possess promising anticancer properties in vitro, triggering biological responses.[1]The ability of NADH/NAD$^+$ couple to act both as hydride donor or acceptor plays an important role in the mode of action of cytotoxic transfer hydrogenation catalysts creating a vital redox pair.So far, the type of organometallic compounds studied for this type of catalysis in cells belong to the arene-metal family.With the aim to design new water-soluble organometallic Ru(II) complexes as catalysts for transfer hydrogenation (TH) reactions with biomolecules, we synthesised four Ru(II) monocarbonylcomplexesof general formula [RuOAc(CO)(dppb)(N^N)]OAc [dppb = 1,4-bis(diphenylphosphino)butane; N^N = picolinamide; 2,2'-bipyridine; 1,10-phenanthroline; pyrazino[2,3-f][1,10]phenanthroline].Our study shows how this class of organometallic ruthenium complexes exhibits good performances in the hydrogenation of NAD$^+$ using HCOOH as hydride source, as well as in the catalytic oxidation of NADH resulting in the formation of the ruthenium hydride derivative, which further reacts with oxygen forming H_2O_2. The rate of both catalytic cycles seems to be critically affected by the type of aromatic nitrogen donor ligand, highlighting a well-defined trend.[2]

Within this work a poly(2-vinyl pyridine)/poly diethyl vinyl pyridine micelle was used as nanocarrier for encapsulation of [Ru] catalysts and the capability of performing TH reactions was studied. The formation of micelles was validated *via* DLSand TEM measurements. Catalytic activity of such micelles was tested for NAD$^+$, benzaldehyde and furfural reduction. The observed catalytic activity ranged from 7 to 20-fold higher for benzaldehydeand furfural reduction in the case of the encapsulated ruthenium compounds in comparison to the unencapsulated ones.This study paves the way to the application of non-arene based organometallic complexes and their possible encapsulation in drug delivery systemsfor targeted cancer therapy exploiting the EPR effect.

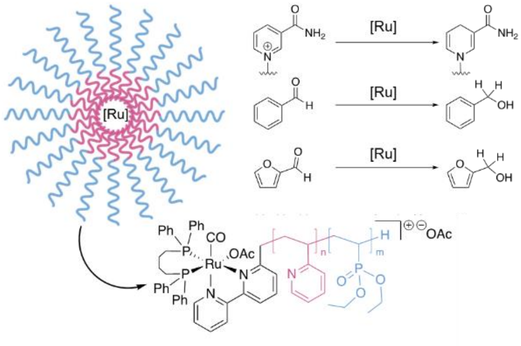

Figure 1. *Transfer hydrogenation reactions performed by novel ruthenium micelles*

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OC14B

INORGANIC CHEMISTRY @SCHOOL: FOSTERING STUDENTS' ENGAGEMENT WITH EDUCATIONAL GAMES AND EXPERIMENTS

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Inorganic chemistry plays pivotal role in energy transition and sustainable development, as global demand for metals increases. A recently published report identifies 34 critical raw materials, corresponding to about 50 elements, with high economic importance for European industriesandhigh supply risk[1]. With the future global resource use projected to double by2030, addressing raw materials' criticality becomes a priority, as well as building an effective dialogue with young citizens. To trigger the students' interest in raw materials, chemistry and sustainability,and promote concepts of circular economy,CNR is strengthening two networks of researchers at national(11 institutes and 15 cities) and European (30 partners from 19 countries) level,working together with students and teachers to create attractive activities and engage them in active learning.In this framework,serious games and hands-on activities based on topics like red-ox reactions, materials production, minerals mining and refining[2] have been set up.*Rawseeker*and*EcoCEO*[3]are two successfully developed board and digital gameswhere players are involved ininorganic chemistry as well as geopolitical and economic dynamics.Hands-on activities were alsopromoted at elementary schools thanks to the peer-to-peer methodology: in *Metals in action*,after a training with researchers, high school students produce communication products and bring highly engaging experiments to primary schools.These approaches will increase awareness of the complexity and interrelation of science, economy with social and sustainability issues.

Figure 1: *"Metals in Action" activity: high school students involve pupils from elementary school in simple but engaging chemical experiments*

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OC15B

STUDIES OF THE HALOGEN ADDITION TO NHC-Au SYSTEMS AND ON THE ANTICANCER ACTIVITY AGAINSTNON SMALLLUNG CANCER CELLS.

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NHC-gold(I) and gold(III) complexes display applications in the field of catalysis and bioinorganic.[1] The conversion of linear Au(I) to square planar Au(III) in N-Heterocyclic Carbene complexes can be achieved by simple addition of elemental halogensor sources of halogens;[2] nevertheless,gold(III) complexes are less common than gold(I) complexes[3]and mixedhalide gold(III) complexesare even less widespread. In this work, to investigate the mechanism of the halogen addition to NHC-Au(I) systems, we considered the iodine or bromine additionto asymmetrically disubstituted1-benzyl or methyl-3-methyl-imidazolyl-2-yl-gold(I)X complexes (where X = Cl, I). As highlighted by the X-ray diffraction of the molecular structures, the iodine addition led to the sole formation of *trans*-NHC-AuClI$_2$while the bromine addition resulted to be strongly case-sensitive, with outcomes depending on the nature of the starting carbene complex, on the on the experimental conditions and on the substituents of the starting NHC ligand (Figure 1). Thestructural and spectroscopic characterizations wereanalysed in terms of the Inverted Ligand Field theory, purposing a mechanism ofhalogen addition to linear complexes of Au(I). Finally, NHC-Au(I) and NHC-Au(III) are potentially very active as anticancer agents.[4]MTT tests were performed to verify the anticancer activity of the NHC-Au(III) and NHC-Au(I) systems on non-small lung cancers cells, the K-RAS well type cells (WT) and mutant (MUT) cells. As an overall result, most of the Au(III) derivatives were found unsuitable for the tests, mostly for instability issues, while1,3-dimethyl-imidazolyl-2yl-gold(I)-triphenylphosphane and 1-benzyl-imidazolyl-2yl-gold(I)-triphenylphosphanewererather active, with the former largely more cytotoxic than the latter. The two active gold compounds, structurally rather similar, displayed diverse activity for the WT and MUT lung cancer cells suggesting specific molecular targets for these gold compounds.

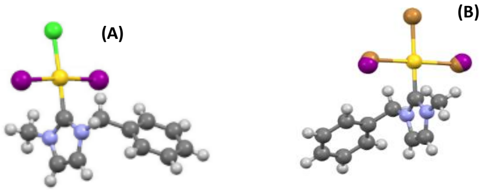

Figure 1: *View of the trans-diiodo-monochloro-gold-(1-benzyl-3-methyl-imidazolyl-2yl)(**A**) and cis-dibromo-monoiodo-gold-(1-benyzl-3-methyl-imidazolyl-2yl) (**B**)*

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OC16B

DEVELOPMENT OF OXALIPLATIN DERIVATIVES: SYNTHESIS, CHARACTERIZATION AND PRELIMINARY IN VITRO ACTIVITY.

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Colorectal cancer (CRC) is the third cancer type for the estimated new cases and deaths in both males and females in the USA[1] and developed countries. Despite recent developments in molecular targeted therapy, chemotherapy still remains the bedrock of CRC treatment, both in the first-line single-agent therapy and in combined regimens such as FOLFOX that associates 5-fluorouracil (5-FU) and oxaliplatin (OX)[2]. OX is a well-known and widely used third-generation platinum-based pharmaceutical, targeting DNA and blocking its replication.

In the search for new, possibly less toxic and more active OX analogues, we have explored the combination of the Pt-binding groups with the stable amino-pyrimidine curcumin moiety. Firstly, several amino-pyrimidine derivatives were synthesized and fully characterized in solution by $^{1}H/^{13}C$ NMR, UV-Vis spectroscopy and mass spectrometry. Then, acid-base equilibria were investigated and preliminary results on biological activity were collected by cell viability assays on different cancer cell lines (HCT-116, HT-29).

The lead compound MPY was linked through an oxopropyl spacer to *N,N* bidentate ligands DAP (1,3-diaminopropane) and DACH (trans-1,2-Diaminocyclohexane) and then complexed with Pt(II) (Figure 1).

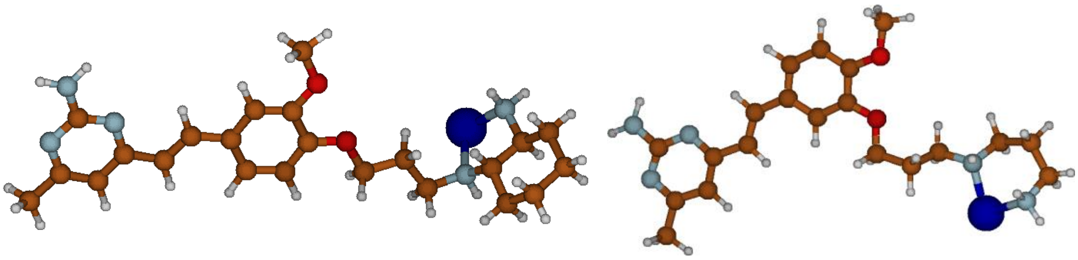

Figure 1: *Selected configurations for complexes PtMPY1 and PtMPY2. Solvent is not shown. (Pt= blue, C=brown, H=light grey, N=light blue, O=red).*

The investigated Pt(II) complexes underwent solution study (NMR, UV-Vis) and DFT calculations. Computations using Gaussian09 with SCRF implicit solvation. The geometry of Pt(II) complexes was optimized at different levels of theory and the shielding constants were computed in order to predict NMR resonances.

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OC17B

NEW CYTOTOXIC GOLD(I)-NHCCOMPLEXES WITH POTENTIAL TARGETED ANTICANCER ACTIVITY

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In recent decades, the attempts to repurpose auranofin as a possible anticancer agent have triggered growing interest in Au-based complexes as promising candidates in the search for new anticancer therapeutic strategies.[1] Although the mechanism of action for which gold-based compounds cause cellular apoptosis in cancer cells has not been completely clarified yet, is commonly accepted that the inhibition of thioredoxin reductase (TrxR) plays a pivotal role.[2] The mitochondria-mediated apoptosis induction presents several advantages, including the potential overcoming of resistance that often occurs after treatment with conventional Pt-based drugs. In order to selectivelydeliver therapeutic agents to the desired site or target within the body, targeting strategies are a valid approach to be explored. Targeting involves the identification of specific molecular biomarkers that are particularly present in cancer cells and designing drugs that can interact specifically with them, to obtain a preferential drug's accumulation and selective activity on cancer cells. In this project, we report the synthesis, characterization and cytotoxicity studies of eight new gold(I) complexes. Two new NHC-based gold(I) complexes bearing a fluorescent probe were initially synthesized, characterized and furthermore conjugated to three selected molecules able to target ovarian cancer cells according to different targeting strategies. Two gold(I) complexes were firstly conjugated with 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranose, a biomimetic glucose substrate, potentially able to increase the metal-complex uptake in tumour cells by exploiting the overexpressed GLUT-mediated transport (Warburg effect).[3] Fluorescence and ESI-MS experiments showed the interaction of the new gold(I) conjugates with human serum albumin (HSA), suggesting the possibility of an HSA-mediated transport in the bloodstream to reach the tumour site. Biological tests on A2780 ovarian cancer cell lines showed a significant enhancement in the cytotoxicity of the complexes when conjugation with 1-thio-β-D-glucose tetraacetate is present. Cellular localization experiments by confocal microscopy confirmed the latter results. Subsequently, the same gold(I) complexes were conjugated with two targeting peptides: *C-βAla-RGD*, which targets the overexpressed integrin receptors on the A2780 cell line, and *CrFrFrF*, a mitochondria-targeting peptide which allows the drug to accumulate in this organelle, where TrxR is mainly present. In this contribution, the cytotoxic activity promoted by the conjugates will be discussed, comparing the results obtained through the three different targeting strategies.

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OC18B

REDUCTION MECHANISM AND G-QUADRUPLEX DNA BINDING OF A REDOX-ACTIVATED PLATINUM(IV)–SALPHEN COMPLEX

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G-quadruplex nucleic acid, obtained by self-assembly of guanine-rich nucleic acid sequences, has recently been considered an attractive target for anticancer drug design. Then, compounds able to bind and stabilize such kind of DNA structures would be greatly beneficial in anticancer therapy. Numerous planar organic small molecules have been studied, as they exhibit many characteristics that enhance the affinity for G-quadruplexes. However, while most of the reported G-quadruplex binding molecules are purely organic structures, metal complexes offer a wide range of electronic and structural properties that can be exploited for designing new drugs capable of interacting with G-tetrads. Here, we present the results of a theoretical investigation on a Pt(IV)-salphen complex with chlorido ligands in the axial position,[1] which, upon reduction to the corresponding Pt(II) species, has the ability to bind G-quadruplexes (Figure 1). Inner- and outer-sphere reduction mechanisms have been investigated using DFT in the presence of classical reducing agents such ascorbic acid and cysteine as model of sulfur-reducing agents. The results demonstrate that both ascorbate and cysteine efficiently reduce the studied complex. To elucidate the targeting and binding mechanism of the G-quadruplex, classical molecular dynamics (MD) simulations have been conducted, revealing the specific interactions involved in recognition. [2]

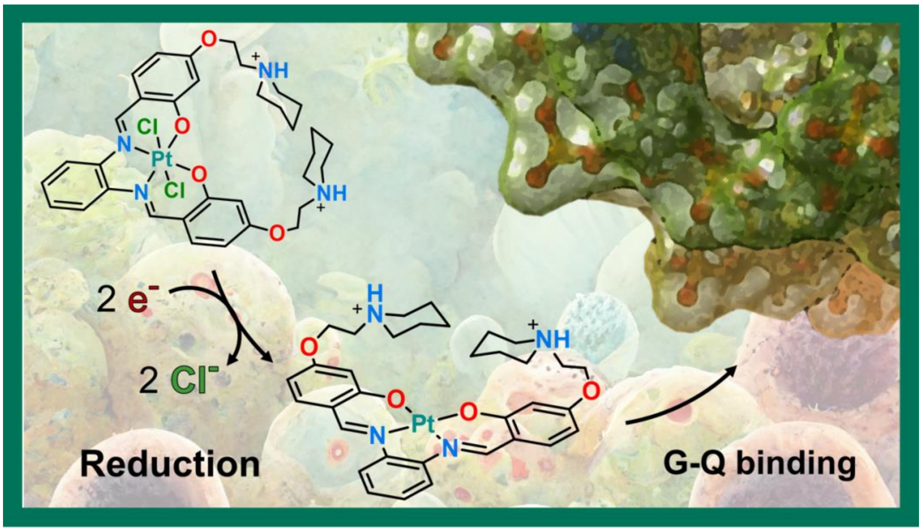

Figure 1: *Mode of action of a new redox-activated Pt(IV)-Salphez*

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OC19B

INCORPORATION OF *N7*-PLATINATED GUANINES INTO THERMUS AQUATICUS (TAQ) DNA POLYMERASE: ATOMISTIC INSIGHTS FROM MOLECULAR DYNAMICS SIMULATIONS

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The mechanism of nucleos(t)ides analogues of incorporation into DNA polymerases, which produces the observed final insertion into DNA, has been extensively investigated.[1-3]In the present study we employed Molecular Dynamics Simulations to gain atomistic insights into the mechanism of incorporation of *N7*-platinated deoxyguanosine triphosphatesin complexes of the type: [Pt(dien)(N7-dGTP)] (**1**), cis-[Pt(NH_3)$_2$Cl(N7-dGTP)] (**2**), and cis-[Pt(NH_3)$_2$(H_2O)(N7-dGTP)] (**3**) {dien = diethylenetriamine; dGTP = 5′-(2′-deoxy)-guanosine-triphosphate}(see **Figure 1a**), using canonical dGTP as a reference, into the model DNA polymerase I from *Thermus aquaticus* (Taq DNA polymerase, **Figure 1b**), in the presence of DNA. Through unbiased molecular dynamics simulations (200 ns for each complex), we have conducted an in-depth analysis of the four ternary complexes, yielding significant findings that enhance the understanding of the available experimental results.[4,5] Our analysis has revealed that complex **1** exhibits considerably lower affinity for Taq DNA polymerase compared to complexes **2-3**. The affinities of cisplatin metabolites **2-3** for Taq DNA polymerase were found to be quite similar to that of natural dGTP, leading to a reduced incorporation rate for complex **1** when compared to complexes **2-3**. In addition, the cisplatin metabolites **2-3** appeared to be easily recognized, giving a Watson–Crick base pairing that strictly resembled that of natural dGTP. This notable disparity between complex **1** and complexes **2-3** suggests that the observed incorporation of complex **1** in previous in vitro experiments may be less significant than that of cisplatin metabolites **2-3**. These findings could have significant implications for the cisplatin mechanism of action, as the high intracellular availability of free nucleobases might promote the competitive incorporation of platinated nucleotides over direct cisplatin attachment to DNA.

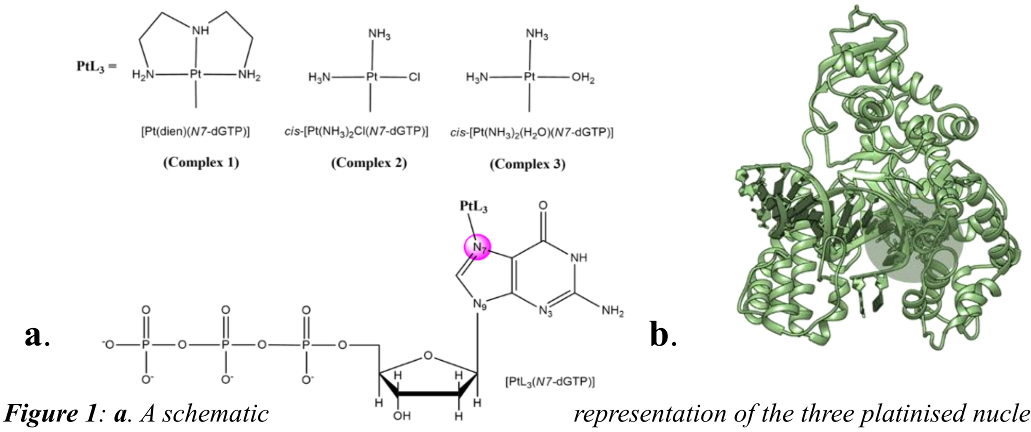

***Figure 1**: **a**. A schematic representation of the three platinised nucleotides studied. **b**. A representation of the secondary structure of the Taq polymerase with DNA.*

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OC20B

SYNTHESIS AND ENCAPSULATION IN NANOPARTICLES OF NEW Pt(IV) COMPLEXES FUNCTIONALIZED WITH MITOCHONDRIA-TARGETING AGENTS

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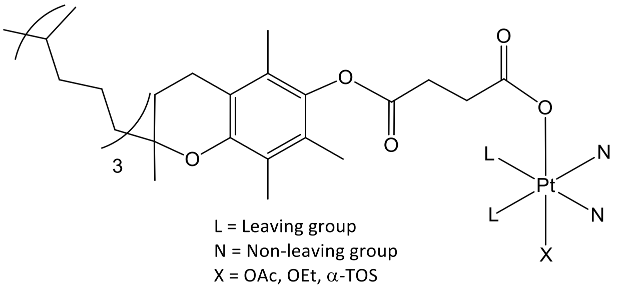
Since its FDA approval in 1978, cisplatin has been one of the most important antitumoral drugs in clinical practice, where it wasemployedfor the treatment of several different types of tumours. Subsequently, other Pt(II) drugswith a similar mechanism of action (namely carboplatin and oxaliplatin) were synthesized and approved for anticancer treatment.[1] However, despite their success, cancer is still one of the main causes of death world-wide. Indeed, the efficacy of these drugs is reduced by development of resistance by cancer cells and by their severe side effects.[2]In light of this, it is clear that we are in high need of new and more effective anticancer drugs. In this frame, one strategy consists in the oxidation of the already clinically approvedPt(II) drugs to their Pt(IV) counterparts. Indeed, Pt(IV) complexes possess several advantages overtheir precursors, such as their improved kinetic inertness, which render them less prone to off-target reactions, and therefore less likely to cause side effects.[3]Moreover, thanks to their octahedral geometry, they possess two additional axial ligands which can be functionalized with bioactive molecules to increase the overall pharmacological action.[4]With this respect,mitochondria-targeting agents, such as α-tocopherol succinate (α-TOS), appear to be very promising candidates for the functionalization of the axial position of these complexes. Indeed, α-TOS can lead cancer cells to apoptosis by disrupting the mitochondrial functionality through the inhibition of some anti-apoptotic proteins.[5] Therefore, a Pt(IV) complex derived from the oxidation of the clinically approved Pt(II) drugs and endowed in the axial position with α-TOS would be a dual-targeting anticancer drug, capable of damaging both the DNA and mitochondria. Moreover, the possibility of encapsulating these complexes in PLGA-PEG nanoparticles, and thus of creating a smart delivery system, can potentially further broaden the clinical applications of these drugs.



L = Leaving group
N = Non-leaving group
X = OAc, OEt, α-TOS

Figure 2.*Schematic structure of the proposed Pt(IV) complexes.*

***Acknowledgements*:**

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OC21B

LIGAND ENGINEERING IN MIL-140A(Ce) METAL-ORGANIC FRAMEWORKS FOR BIOGAS UPGRADING

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Biogas upgrading involves CO_2 removal from raw biogas to produce biomethane, a sustainable biofuel well aligned with international climate goals. Therefore, the development of efficient and cost-effective CO_2 separation technologies to scale-up the production of biomethane is imperative.[1] In this context, an appealing candidate is F4_MIL-140A(Ce), an ultramicroporous Metal-Organic Framework based on Ce(IV) and tetrafluoroterephthalic acid as organic linker (Figure 1). This system exhibits a non-hysteretic step-shaped CO_2 adsorption isotherm whose molecular origin is attributed to a cooperative CO_2 mechanism that involves the concerted rotation of fluorinated aromatic rings.[2,3]
To better understand the influence of fluorination of ligands on the absorption behaviour, we herein report a ligand engineering approach targeting the MIL-140A(Ce) topology and involving terephthalic linkers with different degree of fluorination and isomerism (Figure 1). To this end, we synthesised novel Fx-MIL_140A(Ce) MOFs by means of both an acetonitrile-based solvothermal synthesis and a milder methanol/water mixed solvent approach. The former route led to highly crystalline MOFs having unreacted linkers and fluoride ions trapped in the pores, while the latter allowed to obtain clean materials, although with lower crystallinity. The MOFs were characterized by solid-state NMR techniques that shed light on their local structure, as well as gas adsorption measurements. No step-shaped CO_2 isotherm was observed, unravelling a strong relationship between the fluorination degree of the linker and the adsorption behaviour of the resulting materials. These results open the way to deeper experimental and computational investigations into structure-property relationship which will guide the design of such advanced materials and rationalize their separation performance.

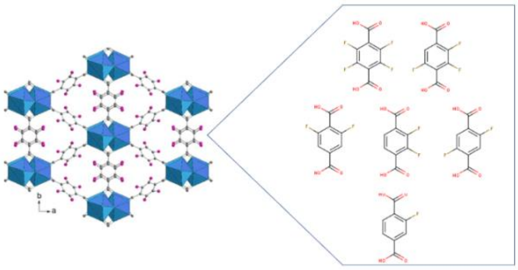

***Figure 1**. Linkers with different degree of fluorination and isomerism used in this work.*

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OC22B

THIAZOLE-DECORATED MOFs FOR DICLOFENAC SODIUM LUMINESCENCE SENSING AND ADSORPTION IN WASTEWATER

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Access to safe water, sanitation and hygiene is the most basic human need for health and well-being. The increase in concentration of Persistent Organic Pollutants (POPs) in waters around the globe is a problem that should be urgently addressed to avoid the possibility of adverse effects on health and the environment. The ideal material for water remediation should combine high POPs adsorption capacity and sensitive light-responsive behavior for selected contaminants. Due to the vast library of nodes and spacers conceivable, MOFs show exceptional chemical and structural versatility combined with permanent porosity and represent the ideal materials for this task.[1] While MOFs featuring fully carbocyclic spacers are ubiquitous, much fewer examples are found with (N,S)-containing heterocycles like thiazole. Thiazoles are electron-deficient systems bearing a basic sp2-N atom and a sp3-hybridized S atom; they are intrinsically fluorescent[2] and they can be found in several naturally occurring biomolecules like luciferin (the active component generating luminescence in fireflies). In this lecture, two representative examples of UiO-67-type MOFs decorated with tailored thiazole-containing linkers will be presented, along with their exploitation in the field of luminescence sensing and adsorption of Diclofenac Sodium in wastewaters (Figure 1).[3,4]

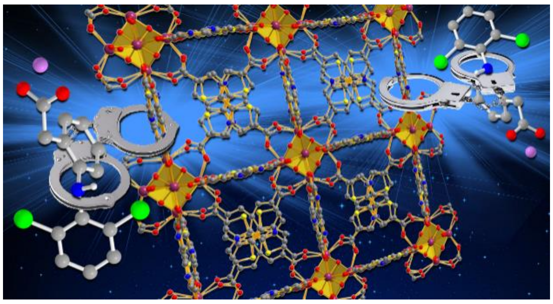

Figure 1: *Diclofenac adsorption by* ***UiO-67-TzTz****. From reference [3].*

Acknowledgements: *The PRIN 2017 Project Multi-e (20179337R7) "Multielectron transfer for the conversion of small molecules: an enabling technology for the chemical use of renewable energy" is acknowledged for support to this work.*

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OC23B

HR-PXRD ADSORPTION ISOTHERMS FOR UNDERSTANDING THE CO_2 ADSORPTION IN AN IRON(III) PYRAZOLATE-BASED MOF

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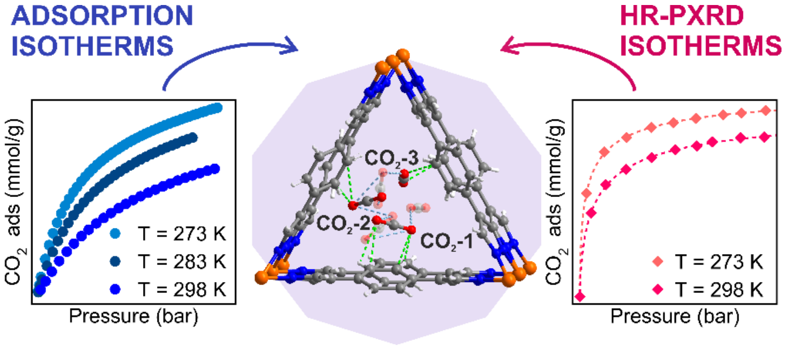
Understanding adsorption processes at the molecular level is essential for a thorough characterization of the pore surface of porous materials and requires adequate techniques.[1,2] In the recent years, *in situ* synchrotron-radiation high-resolution powder X-ray diffraction (HR-PXRD) has emerged as a powerful tool to unveil the primary adsorption sites and main host-guest interactions in various porous materials.[3] Nonetheless, this approach has not yet been brought to the limit. Recent efforts focused on understanding the whole adsorption process, *e.g.* through the construction of PXRD adsorption isotherms, have been made.[4]



This work[5] shows that a plethora of hidden but easily accessible information can be extracted from still underexploited PXRD data without the necessity to rely on single crystals or more sophisticated X-ray based techniques. For this purpose, an in-depth HR-PXRD characterization of the CO_2 adsorption process ($T = 273$ and 298 K, $p_{CO2} = 0$-8 bar) in the robust pyrazolate-based $Fe_2(BDP)_3$[6] [H_2BDP = 1,4-bis(1*H*-pyrazol-4-yl)benzene] metal-organic framework was performed. The behaviour of $Fe_2(BDP)_3$ at the molecular level was accessed by a combination of diffraction experiments as well as computational modelling and compared to that obtained, for the bulk, from "classical" adsorption isotherms. Results from both approaches were juxtaposed with the aim to show that PXRD, applied on variable gas pressure datasets, can be successfully exploited not only to localize the adsorbate in the host framework, but also to shed light on the thermodynamics of the adsorption process.

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OC24B

A NEW REGENERABLE ANILATO-BASED ULTRAMICROPOROUS 3D MOF FOR CO_2 UPTAKE AND SEPARATION

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The combination of a properly designed organic linker, 3,6-N-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone (trz_2An), with Co^{II} ions results in a novel 3D ultramicroporous MOF with high CO_2 uptake capacity and separation efficiency, with particular attention to CO_2/N_2 and CO_2/CH_4 gas mixtures.[1] This material consists of 1D chains of octahedrally coordinated Co^{II} ions linked through anilato ligands at the equatorial positions and triazole substituents from two neighbouring chains at the two axial positions. This leads to a 3D microporous structure with voids with an affinity for CO_2 molecules (Figure 1) and channels that enable the selective entry of CO_2 but not of molecules with larger kinetic diameters such as N_2 or CH_4. Adsorption studies revealed that (i) the MOF presents a remarkable carbon dioxide uptake, above 20% in weight; (ii) CO_2 adsorptive separation is successfully performed in CO_2:N_2 and CO_2:CH_4 gas mixtures, exhibiting high selectivity in a large operation range; (iii) regeneration is easily achieved under mild conditions.

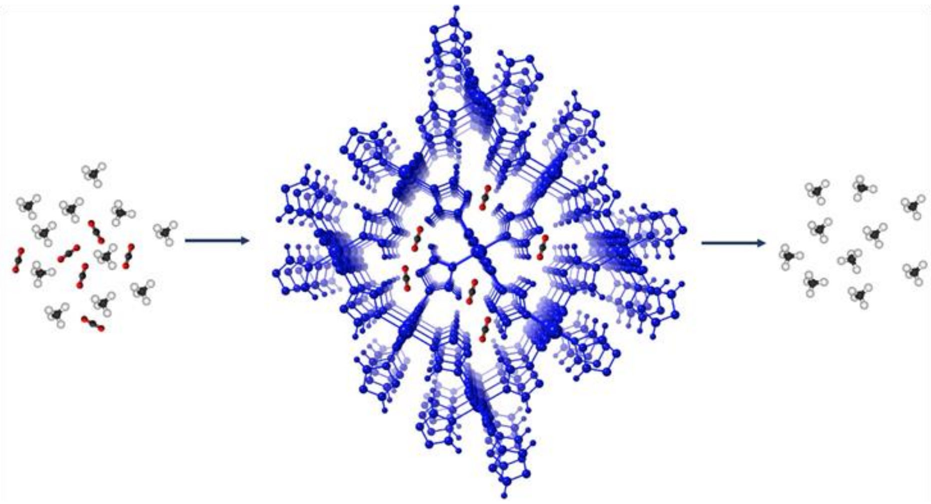

Figure 1. *Schematicrepresentation of CO_2separation*

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OC25B

NOVEL FLUORINATED METAL-ORGANIC FRAMEWORKS FOR CO_2 ADSORPTION AND SEPARATION

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Valentina Crocellà,[3] **Virginia Guiotto**,[3] **Margherita Cavallo**,[3] **Matteo Signorile**,[3] **Lucia Calucci**[4],
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Metal-organic frameworks (MOFs) are a class of porous materials constituted by the ordered connection of metal clusters and organic linkers.[1] MOFs have been widely studied for many gas separation processes, including post-combustion CO_2 capture.[2] Among them, a class of MOFs of particular interest are those featuring phase-change adsorption behavior usually evidenced by steep increase in the adsorbed amount of gas in a narrow pressure region with a peculiar S-shaped adsorption isotherm.[3] We recently reported on a comprehensive study of the CO_2 adsorption mechanism of a perfluorinated Ce^{IV}-MOF, namely F4_MIL-140A(Ce) based on tetrafluoroterephthalic acid and featuring a sigmoidal shape CO_2 isotherm at low relative pressure depending on temperature. We disclosed the complex adsorption mechanism by using several coupled techniques, such as *in-situ* synchrotron high resolution diffraction, FT-IR, Solid state MAS NMR, DFT calculations and calorimetric techniques.[4] The work has been recently expanded through the solvent-free synthesis of other fluorinated MOFs based on Al and perfluorinated aryl and alkyl linkers (i.e. tetrafluoroterephthalic acid and tetrafluorosuccinic acid) and having the MIL-53 type structure. [5] The former exhibits an interesting phase from narrow pore to large pores purely induced by temperature changes. The same behavior has been observed by increasing the pressure range for the CO_2 adsorption. Synthetic procedures, spectroscopic characterization and gas adsorption behaviorof the new synthesized compounds will be also discussed.

Acknowledgements: *Authors thank MIUR trough the Project PRIN 2020 doMino (ref. 2020P9KBKZ)*

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OC26B

TAILORING FERRITE OXIDE NANOPARTICLES FOR CATALYTIC APPLICATIONS

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Magnetic nanoparticles (MNPs) have attracted significant interest in various scientific fields due to their unique magnetic properties and potential applications in biomedicine, electronics, and catalysis[1]. This study focuses on the synthesis, characterization, and coating of mixed ferrite oxide nanoparticles, specifically Nickel-ferrite ($NiFe_2O_4$), Cobalt-ferrite ($CoFe_2O_4$), and Nickel/Cobalt-ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$)[2] (Figure 1).

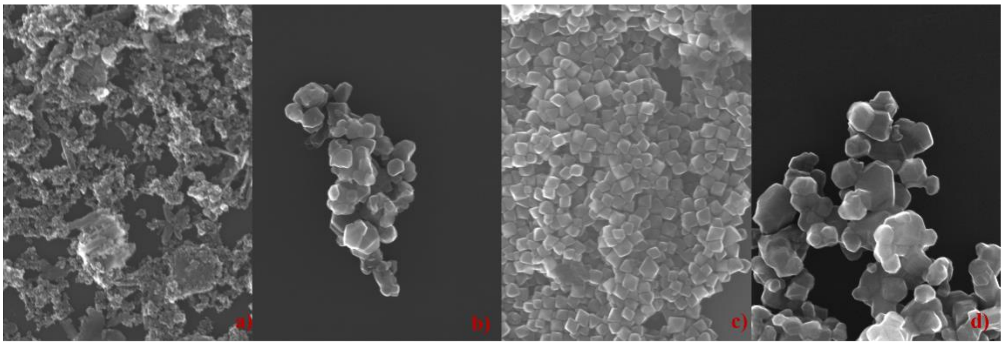

***Figure 1**: STEM images of Fe_3O_4 (a), $NiFe_2O_4$ (b), $CoFe_2O_4$ (c), $Ni_{0.5}Co_{0.5}Fe_2O_4$ (d) nanoparticles, with the same magnification value (50.000K)*

One of the aims of this work was to study how the magnetization changes with the variation of the metal added to the ferrite, and the optimization of a silica coating layer that could uniformly cover the magnetic core, without noticeably affecting its magnetic properties. Moreover, the final goal was to deposit catalytically active metal nanoparticles, in order to use these systems in catalysis, exploiting their magnetic properties not only for the recovery and recycling of the catalyst but, in particular, with the aim of further increasing their activity in magnetothermal applications. In order to understand the structure of these systems, a complete characterization was employed through ATR-IR, XRD, STEM, ICP-MS, BET and AGFM analyses. The magnetic properties of these MNPs make them attractive for a wide range of applications in diverse fields. Our preliminary results obtained in the optimization of synthetic experimental parameters to tune the magnetic properties of nanoparticles and early catalytic activity experiments, will be duly presented and discussed.

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OC27B

CYTOTOXIC DINUCLEAR COPPER(II) COMPLEXES TARGET PHOSPHATE IN THE BACKBONE OF DNA

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Metallodrugs hold an important role in anticancer therapy and are still used for several solid tumors. In particular, cisplatin and other Pt(II)-drugs are the frontline therapeutics for lung, prostate and neck cancers.[1] In the pursuit of safer and more active metallodrugs, the dinuclear copper complex bis(acetato)-(μ-2,7-bis({bis[(6-methylpyridin-2-yl)methyl]amino}methyl)naphthalene-1,8-diolato)-di-copper(II), namely $[(HtomMe)\{Cu(OAc)\}_2]^+$,has been designed and synthetized. Its mode of action differs from that of cisplatin, as the complex is specifically designed to interact with the phosphates of DNA, causing damage to the genetic information.In this contribution, we present an investigation using high-resolution mass spectrometry (MS), tandem MS and infrared multiple photon dissociation (IRMPD) spectroscopy in the 600-1800 cm^{-1} spectral range of complexes formed by reaction of $[(HtomMe)\{Cu(OAc)\}_2]^+$with H_3PO_4, 1,2-ethylenediphosphonic acid (1,2-POH_2), 1,4-butanediphosphonic acid (1,4-POH_2), deoxyadenosine monophosphate (dAMP) and deoxyguanosine monophosphate (dGMP). By comparing the structural features revealed by IRMPD spectroscopy with linear IR spectra of the lowest energy structures, we can identify diagnostic signatures of the binding modes between the dinuclear copper(II) complex and phosphate groups.Thesefindingssuggest that the prevailing interaction of $[(HtomMe)\{Cu(OAc)\}_2]^+$ with the phosphate groups in DNAmay contribute to its observed anticancer activity.

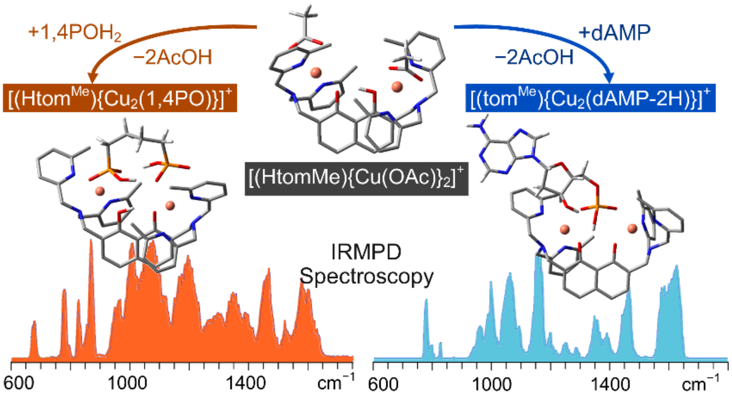

***Figure 1**: Scheme of the reaction of $[(Htom^{Me})\{Cu(OAc)\}_2]^+$with 1,4$POH_2$and dAMP. The IRMPD spectra of the products$[(Htom^{Me})\{Cu_2(1,4PO)\}]^+$and $[(tom^{Me})\{Cu_2(dAMP\text{-}2H)\}]^+$ are reported together with their attributed optimized structures at the B3LYP level. The structure of the starting ion $[(Htom^{Me})\{Cu(OAc)\}_2]^+$is also shown.*

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OC28B

MECHANISTIC INSIGHTS INTO THE FERROXIDASE AND BIOMINERALIZATION PROCESSES IN HUMAN FERRITINS

Cecilia Pozzi,[1] Silvia Ciambellotti,[2,3] Caterina Bernacchioni,[2,3] Veronica Ghini,[2,3] Flavio Di Pisa,[1] Giusy Tassone,[1] Paola Turano,[2,3] and Stefano Mangani[1]

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Ferritins are ubiquitous multimeric protein systems showing a nanocage structure able to include thousands of iron atoms as oxoferric biomineral. In mammals, these twentyfour-mer protein shells are generally heteropolymers composed by two different types of subunits classified, according to their relative molecular weight, as heavy, H, and light, L (183 and 175 amino acids, respectively, in human chains). H chains are deputed to ferroxidase activity, in which Fe(II) is oxidized to Fe(III) in the presence of dioxygen inside the ferroxidase site; on the other hand, L-type chains are involved in iron biomineralization facilitated through a nucleation site, located on the internal cage surface. In humans and other mammals, a further type of ferritin was identified, namely the mitochondrial ferritin (MTF). Besides the high structural conservation of the catalytic center, the mechanism by which the ferroxidase reaction occurs is not fully understood. To gain insights in this catalytic reaction, we developed a soaking/flash freezing method allowing aerobic and anaerobic addition of Fe(II) to ferritin crystals and multi-wavelength anomalous diffraction was exploited to unambiguously detect iron atoms.[1-5] Through this method we observed for the first time the iron binding sites in X-ray crystal structures of human H ferritin (HuHf) and human MTF (hMTF) and how they become populated with time.[2,5] Interestingly, accessories transient metal sites were also identified in the proximity of the ferroxidase site and demonstrated to play a key role in the reaction turnover.[2,5]
Furthermore, through a time-dependent series of X-ray crystal structures of iron-loaded human L-ferritin (HuLf) we observed the progressive formation of (μ^3-oxo)tris[(μ^2-peroxo)(μ^2-glutamato-κ*O*:κ*O*')](glutamato-κ*O*)(diaquo)triiron(III) anionic clusters on the inner cage surface.[6] The functional significance of the protein carboxylates involved in the coordination of the metallocluster for biomineralization was clearly demonstrated by the lower iron oxidation rate measured in the HuLf triple variant E60A-E61A-E64A.[6] In a subsequent study, we observed the growth of this initial seed to form an octa-nuclear iron cluster, highlighting the key role played by the glutamate residues on the inner cage surface.[7] Similar metalloclusters were also observed in horse spleen ferritin, suggesting that it constitutes a common feature of mammalian ferritins, the nucleation site of L-type proteins.[6,7] Our results, combining structural and stopped-flow kinetic data, provide new import clues to explain the ferroxidase and biomineralization processes in vertebrate ferritins.

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OC29B

AN ESI-MS STUDY TO GAIN AN INSIGHT ON THE INTERACTIONS BETWEEN MERCURY COMPOUNDS AND PROTEIN FREE THIOLS

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Mercury (Hg) is an ubiquitous heavy metal found naturally in the environment, and it is considered to be one of the most toxic elements to humans. Mercury compounds have been used for centuries in a wide variety of applications, including medicinal and industrial use. According to the report of the United Nations Environment Programme (UNEP), around 2220 tons of mercury emissions were seen in 2015 from anthropogenic sources and it is regarded as a dangerous pollutant in the globe[1]. The well-known toxic effects due to Hg exposure represent a critical concern for public health. Multiple mechanisms of Hg toxicity have been reported, such as enzyme inactivation and oxidative stress[2]. However, the precise molecular mechanisms of toxicity of mercury compounds have yet not fully disclosed.

Here, we have investigated the interactions of a few selected mercury compounds with a group of model proteins through an advanced ESI MS approach, which turned out particularly informative in revealing the nature of protein bound metallic fragments. The panel of Hg compounds comprises Thimerosal, mercury(II) Cloride, phenylmercury and methylmercury. Because of the high affinity of mercury towards sulfhydryl (-SH) groups[2], these mercury compounds were reacted with free thiol of several proteins, namely Human Serum Albumin (HSA), superoxide dismutase (SOD), human carbonic anhydrase I (hCA1), ribonuclease A (RNase A), and C-terminal dodecapeptide mimicking the TrxR1 active site (dTrxR).

Generally, the analysis of the obtained mass spectra revealed the formation of stable adducts between Hg compounds and proteins and allowed us to characterize the nature of the different Hg fragments that bind the proteins.

Overall, the present results set the stage to better understand the mechanism of action of these mercury compounds and elucidate at the atomic level their mechanism of interaction with proteins and peptides.

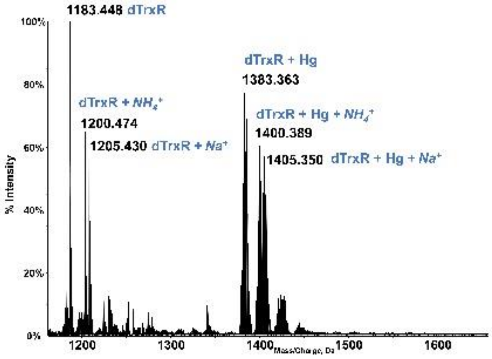

***Figure 1**: Multicharged ESI-Q-TOF spectra of dTrxR 5 × 10^{-6} M in 20 mM of ammonium acetate solution at pH 6.8 and incubated at 37°C for 24 h with Thimerosal*

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OC30B

CONTROLLING THE REDOX STATES OF COPPER RADIOISOTOPES FOR CANCER IMAGING AND THERAPY: COORDINATION CHEMISTRY TO THE RESCUE

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Ifproperly harnessed, the radiation emitted by copper radioisotopes can be exploited to image, treat, and monitor cancer. For *in vivo* applications, the radiation must be uniquely delivered to the cancer site by trapping the radioisotopes in a thermodynamically stable and kinetically inert complex formed with a chelating agent, in turn attached to a tumour-seeking vector.However, the biologically triggered Cu^{2+}/Cu^{+}redox conversion is a possible decomplexation pathway that may occur *in vivo*.[1] To hamper this phenomenon, we have developed a series of macrocyclic chelators containing donors with diverse chemical softnessable to stabilize both oxidation states.[1,2] Nevertheless, when only N and S donors were inserted on 12-, 13-, or 14-member macrocycles, a marked $[^{64}Cu]Cu^{2+}$release was found in human serum, likely as a result of the non-fully saturated coordination sphere generated around Cu^{2+} that can create open-labile sites, fostering the binding of competitive species.[3]To improve the integrity of the resulting $Cu^{2+/+}$ complexes in biological environment, we have hypothesized that a smaller macrocyclic backbone could slow down the observed demetallation by fully encapsulating the copper ion and saturating its coordination sphere. We have therefore designed a new ligand, 1,4,7-tris[2-(methylsulfanyl)ethyl)]-1,4,7-triazacyclononane (NO3S), by inserting three sulfanyl pendants on a 9-member ring N_3backbone.[4]Herein, the solution behaviour of NO3S and the coordination chemistry of its $Cu^{2+/+}$ complexes in aqueous solution and in the solid state will be presented.

Our results indicated that pH-depending stable mononuclear species are formed in aqueous solution when Cu^{2+} is bound to NO3S and that Cu^{2+} resulted fully embedded in the ligand cleft in a hexacoordinated N_3S_3 environment.NO3S possessed the remarkable ability to stabilize Cu^{+} forming a species where all the donors are involved in the coordination sphere. While radiolabeling studies pointed out the exceptional affinity of NO3S towards $[^{64}Cu]Cu^{2+}$, human serum stability assays revealed the increased integrity of $[^{64}Cu][Cu(NO3S)]^{2+}$ when compared to the previously considered S-containing macrocycles. This outcome confirmed the initial hypothesis that a fully encapsulated metal ion affords a more inert complex in the presence of competitive ligands.[4]

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OC31B

SCANDIA EFFECT ON ZIRCONIA BASED ELECTROCHEMICAL SENSORS FOR THE DETECTION OF DIHYDROXYBENZENE ISOMERS

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In recent years the interest in materials such as zirconium oxide has undergone a new interest. This depends on the good properties of this metal such as a high electrical capacity and excellent stability of their chemical and physical properties (for example, chemical inertia, thermal stability, etc.)[1].

Pure ZrO_2 has low conductivity due to its three structural phases (monoclinic, tetragonal and cubic) and a few oxygen holes. To improve its properties, it is often drugged with rare earth elements such as Yb, Eu, Y, Sc, etc.[2]

Few examples of using only zirconium oxide doped with a rare earth and exclusively for gas sensors are reported in the literature[3].

In this work, we used commercial zirconium oxide doped with 10% Scandia ($ZrO_2$10Sc) without further conjugation with other nanomaterials for simultaneous determination of Hq, Cat and Rs.

Phenol isomers (DHB) are water pollutants and therefore can cause serious diseases such as cancer, kidney damage and death in humans[4], as well as high toxicity in animals and plants[5]. Sensitive, fast and easy detection of DHB is essential for health.

In this work we wanted to characterize the commercial samples of pure and doped zirconia with different techniques (SEM, XRD, FT-IR, etc) to study their morphologies and physical characteristics. We investigated the ability of pure ZrO_2 and ZrO_2 doped with yttrium (8mol%) and scandia (10mol%) to simultaneously detect the three isomers of DHB. Our results showed that the sensor composed of ZrO_2*Sc_2O_3 (10mol%) has the best separation performance in terms of selectivity and sensitivity. In addition, the study provides a valuable proposal for the formation of simple and low-cost sensors, since they are derived from a commercial product and are not derived from complicated synthesis processes, which is therefore a guarantee of uniformity and repeatability of the sensitive material used.

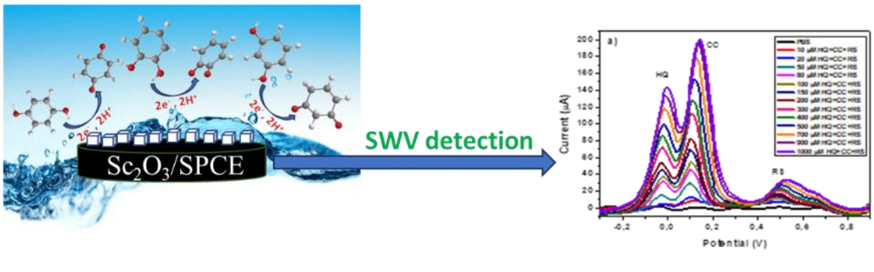

***Figure 1**: Representation of the simultaneous response of Hq, Cc and Rs with the $ZrO_2$10Sc/SPCE sensor.*

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OC32B

FERRITIN AS A NANOCARRIER FOR THE TARGETED DELIVERY OF METAL-BASED DRUGS

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Human-heavy chain ferritin (HuHf) may serve as a nanocarrier for the targeted delivery of anticancer metallodrugs against cancer cells. HuHf is a recombinant protein composed of 24 H-subunits that self-assemble to form a nanocage that is recognized by the transferrin receptor-1 (TfR1), which is overexpressed in different cancer cell lines.

Here we propose ^{1}H e ^{19}F NMR as complementary methods to study the cellular behaviour of metal drug-ferritin conjugates. ^{1}H NMR is used as a tool to characterize the cellular mechanisms of action of the bioconjugate with respect to the free metal-drug in solution [1-2]. Information on the main biochemical pathways as well as on the protein targets of both ferritin-drug conjugate and free drug can be obtained and compared. ^{19}F, instead, can be used as a tool to characterize the cellular behaviour of the ferritin-based nanocarrier itself [3], i.e., to characterize the cellular uptake of the nanocage and to monitor the release of metallodrugs bound to the cage.

Significant examples for both cases will be provided.

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OC33B

THE RANOSTIC NANOPARTICLES IN BNCT

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The development of new accelerator-based neutron sources has given a huge stimulus to the development of new drugs and treatment technologies using boron neutron capture therapy (BNCT). BNCT is a binary chemio-radiotherapeutic modality, early proposed to treat cancer, based on the accumulation of ^{10}B containing agents followed by neutron irradiation[1]. It has been estimated that about 10^{910}B atoms per tumour cell are needed for an effective treatment of cancer. One of the main advantage of this approach is that administering boron and producing alpha radiation selectively in diseased cells, it can kill the pathological ones while sparing the surrounding healthy tissues. However, the expected efficacy has been compromised by the nonspecific biodistribution and rapid metabolism of the clinically used BNCT agents. The aim of this study, is to describe the ability of biodegradable polymers such as poly-lactic and glycolic acid[2] (PLGA), Low Density Lipoprotein (LDL) to deliver boron clusters such as carboranes efficiently and specifically to the pathological tissue. In fact, nanoparticles can improve the pharmacokinetics of BNCT agents, achieving an appropriate tumour to blood ratio. Moreover, the use of a non-invasive imaging method to quantify the boron concentration in the tumour before irradiation is also needed for the timing treatment optimization. To this purpose, theranostic systems, that combine delivery of drugs and imaging agents within a single non-toxic and biodegradable nanovector, represent one of the most promising option. The nanoprobes were tested for the treatment of different tumours and in particular for pulmonary metastasis and mesothelioma. Against these tumours, conventional radiotherapies have limited effectiveness due to the presence of several radiosensitive tissues, which limit the maximum dose deliverable to the malignant nodules. The advantage of BNCT is that it can potentially affect only tumour cells with a lethal dose of radiations, even in case of spreading and infiltrative cases. Finally, BNCT has been recently proposed as a completely alternative and revolutionary strategy to address Alzheimer's Disease treatment. Preliminary results, showing structural damage of beta-amyloid (Aβ) aggregates induced by ionizing radiations generated by neutron capture, will be also described.

***Acknowledgements**: The research leading to these results has received funding from AIRC under IG 2019—ID. 23267 project and from the European Union's Horizon 2020 research and innovation programme under grant agreement 964934 Nectar*

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OC34B

THE STRUCTURE DRIVES THE SHAPE: SYNTHESIS OF TAILORED METAL OXIDE NANOPARTICLES IN GREEN INNOVATIVE MEDIA

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The "template effect" is one of the most important features employed to impart specific shapes to nanomaterials, which may result in tailored technological properties. In this contribution, we describe various examples on how the choice of the synthesis pathway deeply influences the fate of the results, either in the actual composition of the product or in the different morphologyobtained. After a thorough survey of the manifold (co)precipitation and sol-gel methods explored, that led to nanometric zinc oxide nanoparticles endowed with variable colour luminescence, and of the remarkable results achievable when the latter are employed in sensors for pesticide assays, a look will be taken at new classes of solvent media developed in the last decades, likeionic liquids (IL) and more recently Deep Eutectic Solvents (DES). These systems possess nano-homogeneities in their internal structure, mainly leading to the nanosegregation of domains of different polarity (ionic/charged vs apolar moieties), that can be successfully used to achieve a template effect. A further added value of these liquid systems, particularly of DES prepared from raw materials of natural origin (sugars, alcohols, carboxylic acids), is their very benign character and often their recyclability, and the simplicity of their preparation, that often requires only the mixing of solid salts/liquids with little or no heating. Several examples of metal salt nanoparticles synthesized in water-based media, in type III/IV/V DES and in choline ionic liquids will be shown, going from zinc-based systems - oxides and layered composites, like Layered Hydroxide Salts (LHS) - to copper and iron oxides. The prepared materials have different dimensions and adoptvarious morphologies, like spherical, sheet or flower-like shapes[1], and in some cases show remarkable luminescence spectra with a strong and reversible temperature dependence[2].

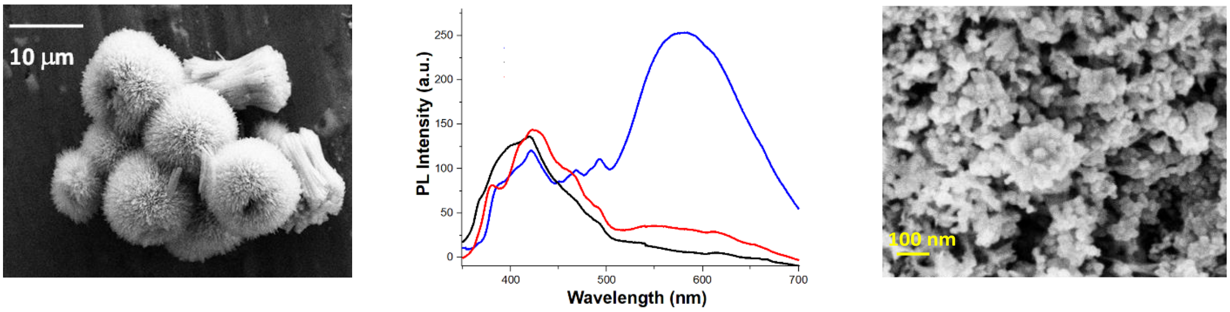

***Figure 1**: Left: Dandelion-shaped CuO; middle: luminescence spectra of ZnO and ZnOCl NPs; right: flower-like ZnO*

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OC35B

PRUSSIAN BLUE NANOPARTICLES: FDA-APPROVED NANOMEDICINE TOOLS WITH UNEXPLORED STABILITY AT PHYSIOLOGICAL pH

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Prussian Blue (PB) is an iron containing coordination polymer, known since the 18th century. Recently, interest has risen for the potential biomedical applications of PB in nanometric form in the fields of imaging and therapy. PB is FDA approved as an antidote for Tl^+ and Cs^+ poisoning, intended for oral use at the acidic pH of the stomach and of most of the intestine track. However, based on FDA approval, a huge number of papers proposed the use of PB nanoparticles (PBnp) under "physiological conditions", meaning pH buffered at 7.4 and high saline concentration. While most of these papers report that PBNP are stable at this pH, a small number of papers describes instead PBNP degradation at the same pH values, i.e. in the 7–8 range.

We thus decided to study the stability of PBNP and demonstrated that they are intrinsically unstable at pH 7.4, due to the formation of OH^- complexes with the kinetically labile Fe^{3+} ions.[1]

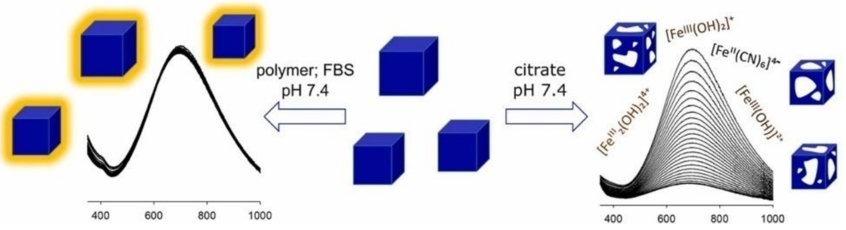

***Figure 1**: PBNP stability in presence of a stabilizing agent or in serum-containing media vs stability in a simple pH 7.4 medium. Figure adapted from ref. 1*

Stability, on the other hand, increases when a stabilizing agent is added during the synthesis or post-synthesis. Moreover, under "physiological conditions" obtained with serum containing media, a protein corona is rapidly formed on the PBNP, preventing degradation of the nanoparticles. The viability of different cell types (i.e. EA.hy926, NCI-H1299, and A549 cells) was also studied in the presence of PBNP, showing, as expect, a good biocompatibility of this nanomaterial.

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POSTERS

P1

EXPLORING HALOGEN BONDING IN THE CO_2-TO-CO REDUCTION BY IRON PORPHYRINS

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Nowadays, problems related with global warming and atmospheric pollution are encouraging scientists to find solutions that could decrease CO_2 levels in the atmosphere, like its conversion, by green strategies, intovaluable reduction products such as CO, HCOOH, CH_3OH, CH_4. Two different strategies can be applied: i) the use of direct sunlight coupled with photochemistry strategies, and ii) the conversion of light into electricity in photovoltaic cells and then, the electrochemical reduction of CO2 by the generated electrons. Due to the inertness of the CO_2molecule, the use of a catalyst to drive its photo- or electrochemical reduction is mandatory, and a great challenge for chemists is to develop selective, efficient, and stable catalysts. Iron(III) porphyrins, when electrochemically reduced to the iron(0) species, are among the most efficient molecular catalysts for the CO_2-to-CO conversion in aprotic solvent (DMF, ACN), in terms of efficiency, catalytic rate and robustness.[1,2]One of the biggestadvantages of porphyrins is that their propertiescan be artfully tuned by tailoring the chemical structure of the macrocycle.[3.4] In this regard, the appropriate substituents in *meso* or *β-pyrrolic* position allows to set up *through-space* or *through-structure*interactions that can favour the catalyst-substrate interaction and adjust the electrochemical propertiesof the porphyrins.

In this contribution, in order to study the macrocycle-CO_2interaction, we present a new set of porphyrins whose chemicalstructureshave been carefully designed to favour *through-space*interactions via halogen bonding. Our main aim is to establish if this kind of weak interaction, which has been never considered before, can have a positive impact on the synergy between the catalyst and the substrate similarly to what has already been demonstrated for other weak interactions (like hydrogen bonding and coulombic interaction) (*Figure 1*).[5,6]The studied compounds present also different substituents in the other *ortho* or *para* positions of the porphyrin phenyl rings, in order to tune both the σ-hole of the halogen atom and the reduction potentials of the Iron centre via *through-structure* interactions.

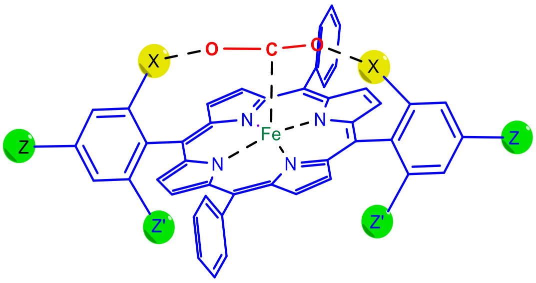

Figure 1*: through-space interaction between porphyrin-based catalyst and CO_2*
X = halogen atom, Z, Z' = substituents able to give through structure effects.

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P2

DIPHOSPHINE RUTHENIUM COMPLEXES IN TRANSFER HYDROGENATION OF CARBONYL COMPOUNDS DERIVED FROM LIGNIN AND BIOMASS IN WATER WITH HCOONa:HCOOH

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Valorisation of lignin and biomass derived carbonyl compounds is increasing its importance in green chemistry, but still represent a challenging task.[1,2] Ruthenium based diphosphine complexes are well known to be active in C-H activation reactions such as transfer hydrogenation in isopropanol/isopropoxide system.[3] In this work, the synthesis of [Ru(X)(dppe)(CO)(phen)]X (X = AcO^-, $PivO^-$, Cl^-, I^-; phen = 1,10-phenanthroline) is described. The compound [Ru(AcO)(dppe)(CO)(phen)]AcO easily reacts with HCOONa in water to form a stable Ru-H species, which displays catalytic activity in transfer hydrogenation reaction for reduction of aldehydes and ketones derived from lignin and biomass. The catalytic activity has been studied on several substrates in water media with 20% MeOH, using different HCOONa:HCOOH ratios, at various temperatures. In particular, substrates such as vanillin, which contains a phenolic group in *para* position to the carbonyl, can undergo a hydro-deoxigenation reaction affording the CH_3 group in place of the CH_2OH. Preliminary results indicate that the reaction can be controlled by temperature.

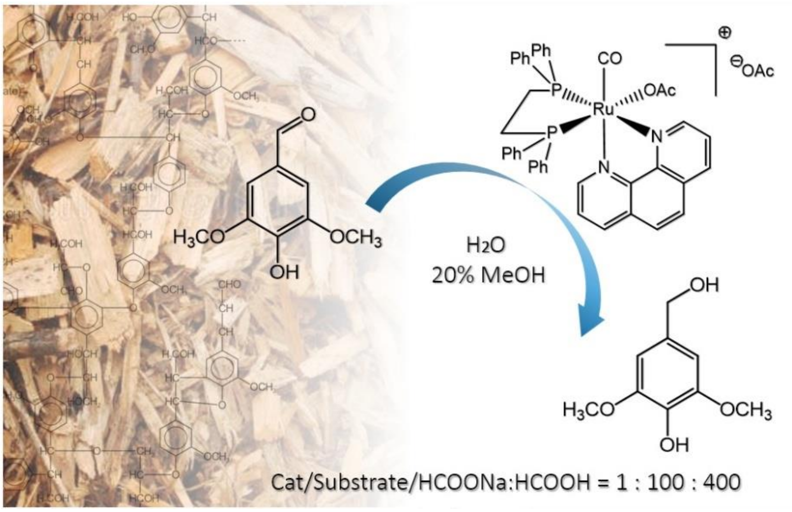

Figure 1

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P3

SYNTHESIS, CHARACTERIZATION, AND BIOLOGICAL EVALUATION OF IMIDAZOLE/BENZIMIDAZOLE PLATINUM DERIVATIVES AS POTENTIAL ANTICANCER AGENTS

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Platinum-based drugs have been known for decades and have been widely used for cancer treatment. However, the problems associated with these traditional complexes are high toxicity, low water solubility, and intrinsic or acquired resistance of some tumors, which limit their activity [1]. To overcome these limitations, the ligands' choice is very important. Indeed, ligands can promote the targeting of tumor cells, possibly without affecting healthy cells. Imidazoles are ubiquitous in nature and play a unique role in the human body [2]. Similarly, 1,10-phenanthroline has special properties due to its peculiar structural features like enhanced intercalating ability and hydrophobicity [3]. Therefore, in the here studied complexes, we chose to use both imidazoles and 1,10-phenanthroline ligands, by synthesizing new cationic monofunctional platinum(II) complexes of the type: $[Pt(\eta^1\text{-}C_2H_4OEt)(NH_3)(phen)]Cl$ (**1**),[4]$[Pt(\eta^1\text{-}C_2H_4OEt)(1\text{-hexyl-1}H\text{-imidazole})(phen)]Cl$ (**2**) and $[Pt(\eta^1\text{-}C_2H_4OEt)(1\text{-hexyl-1}H\text{-benzo[d]imidazole})(phen)]Cl$ (**3**) (**Figure 1**).Interestingly, the cationic nature of **1-3** complexes and their water solubility, compared to cisplatin, make them possible substrates for cell plasma membrane transporters. These monofunctional complexes could form sterically hindered adducts with DNA interfering with DNA/RNA polymerases, as previously observed for other monofunctional Pt(II) complexes [5]. The newly synthesized complexes were characterized by nuclear magnetic resonance (NMR) spectroscopy, and their anticancer activity was assessed by sulforhodamine B (SRB) assay on cancerous (HeLa and Caki-1) and healthy cell line (HK-2). Complex **3** was found to be a promising antitumor agent when tested against HeLa cell line, because showing a cytotoxicity level higher than that of complexes **1**, **2,** and cisplatin.

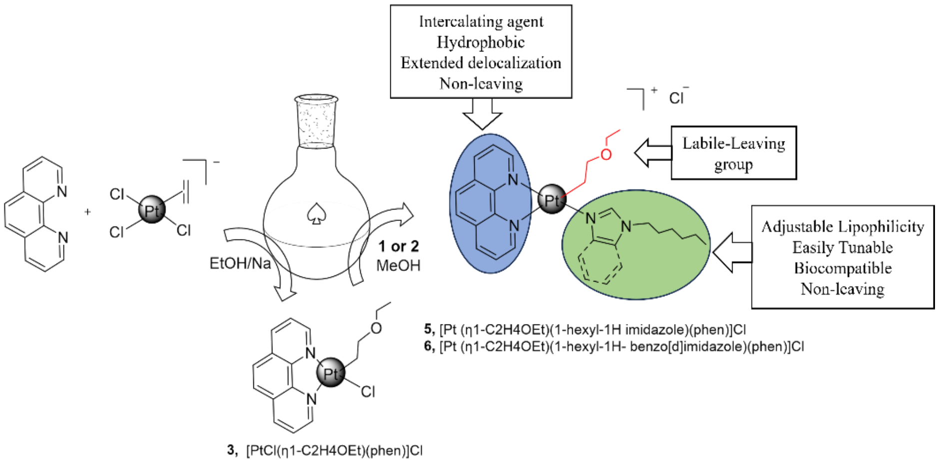

***Figure 1**: Showing the synthetic route and properties of attached ligands with platinum*

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P4

HARNESSING THE ELECTRONIC STRUCTURE OF THE ACTIVEMETAL TO LOWER THE OVERPOTENTIAL OF THEELECTROCATALYTICOXYGENEVOLUTIONREACTION

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One of the main path ways to produce molecular hydrogenis electrochemical water splitting.[1] To increase the efficiency of this process, the overpotential for the oxygen evolution reaction must be minimized. This can be achieved through the use of electrocatalysts. [2] Among the numerous families of catalysts studied and optimized over the years with this purpose, coordination polymers (CPs) recently gained great attention.[3] In this work, we initially defined an accurate computational protocol for the study of electrocatalytic processes on one-dimensional CPs containing first-rowtransition metals (Mn, Ni, Co, Fe). The protocol was experimentally validated and then used to shed light on the role of cooperativity, spin crossover effects, and metal oxidation of these systems towards water oxidation.

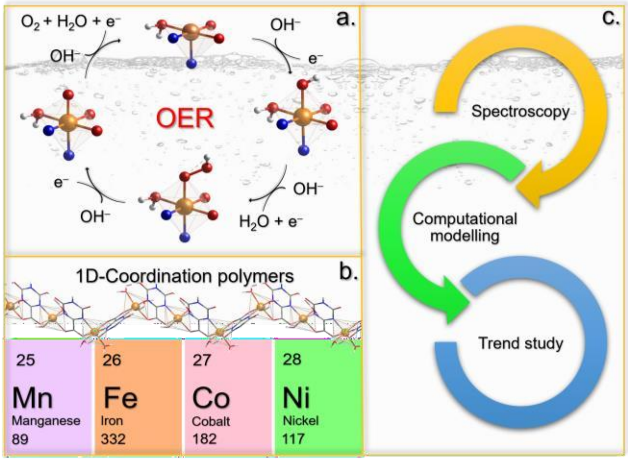

Figure 1*: a) Catalytic OER mechanism in alkaline conditions. b) Schematic structure of the 1D-CPs c) SynergisticapproachtoexploreCPsactivitytowardsOER.*

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P5

THE HEAL ITALIA PROJECT FOR THE DISCOVERY OF NEW METALLODRUGS: TRANSITION METAL COMPLEXES OF SCHIFF BASE LIGANDS AS G-QUADRUPLEX DNA BINDERS

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In the search of DNA-binding molecules with preferential affinity toward G-quadruplex (G4) compared to double-helical DNA, we have recently designed and synthesized several Schiff base complexes of transition metal ions.[1-3] The DNA binding has been studied by using both experimental and computational approaches. G4-DNA sequences are found in several portions of human genome, such as oncogene promoters and telomeres, becoming important anticancer targets. Some of these metal compounds have shown *in vitro* biological activity against human cancer cell lines, that was related to the inhibition of the DNA properties. Besides the important role of the metal ion in determining the DNA-binding strength, the nature of aromatic ring on the N,N' bridge of the Salen scaffold (Fig. 1a) and of positively charged side chains allow to opportunely tune the DNA-binding properties of the resulting metal complexes. In this context, we have recently found that a Cu^{2+}Salphen-like complex (Fig. 1b) shows interesting catalytic activity for the selective epoxidation of styrene. Since analogous transition metal complexes are also effective and selective G4-DNA binders, we are currently investigating the possible catalytic oxidation of guanine DNA bases into 8-oxoguanine, and how this may affect the G4-DNA structure and stability. This study is part of the recently endorsed "HEAL ITALIA" project, which belongs to the broader framework of the Italian National Recovery and Resilience Plan (PNRR). The primary aim of HEAL ITALIA is to create innovative, cost-effective, and non-invasive methods for improved prediction, detection, and monitoring of complex diseases. The collaborative effort of experimental and computational techniques plays a crucial role in achieving this objective.

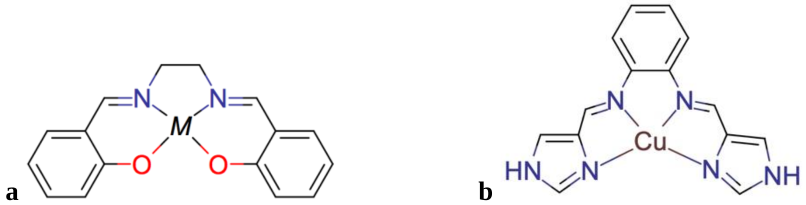

***Figure 1**: Structure of a generic Salen metal complex (a) and of a Cu^{2+}Salphen-like complex (b)*

***Acknowledgements**: We are grateful to the European Union Next Generation EU through the Italian Ministry of University and Research under PNRR M4C2I1.3 Project PE_00000019 "HEAL ITALIA" CUP (B73C22001250006).*

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GOLD NANORODS DERIVATIZED WITH BINARY SURFACTANT MIXTURES: HOW TO SELECT THE SECONDARY SURFACTANT TO OPTIMIZE SHAPE AND SIZE?

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Anisotropic nanoparticles have recently attracted much attention due to their size- and shape-dependent optical properties. Rod-shaped nanoparticles are particularly interesting since they display two plasmon bands: a transverse plasmon band corresponding to an electron oscillation along the short axis of the rod, at around 510–550 nm for gold nanorods (AuNRs), and a longitudinal plasmon band, in the range 600–1200 nm. Indeed, the nanorods' aspect ratio can be modified by the strict control of the experimental parameters during their chemical synthesis, allowing to opportunely tune the position of the plasmon bands, for example obtaining nanomaterials active in the NIR, which is of major interest for applications as therapeutic/imaging ("theragnostic") agents. Another characteristic of anisotropic nanoparticles is their size-related SPR tunability; for example, AuNRs can experience a 50 nm red shift of the longitudinal plasmon mode for a change in aspect ratio (i.e. length/diameter) from about 2.5 to nearly 3; this is a considerable shift, since for spherical AuNPs a ~ 50 nm shift requires a diameter size modification from 10 to 100 nm [1]. Moreover, NRs optical properties (optical absorption or scattering wavelengths) strictly depend on their length and are insensitive to their diameter [2]. If these considerations concur to substantiate the appealing of AuNRs, they also introduce a central issue in their design and synthesis, that is the ability to finely control their aspect ratio, homogeneity and dispersion, since the plasmonic optical properties are much sensitive to these parameters [3]. To attain this goal, a key step is the as accurate as possible comprehension of the mechanism driving the anisotropic growth that is at the base of NRs formation. Since "There is strong experimental evidence that every ingredient/parameter in the synthesis procedure plays a critical role in determining the shape and resulting surface chemistry" [4], the comprehension of the role played by each participant to the synthetic path has been and still is subject to much experimental and theoretical research.

Here, we present the investigation of the molecular, electronic, chemical structure and morphology of gold nanorods prepared with two different secondary surfactants: the weak reducing agents ascorbic acid (AA) and hydroquinone (HQ). The two series of AuNRs differ from plasmon band position, morphology and aspect ratio in a reproducible way, due to the influence of the different secondary surfactants on the anisotropic growth process. Our investigation aims at opening new perspectives about the possibility to design AuNRs of desired aspect ratio and shape by opportunely selecting the secondary surfactant.

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P7

THE BENEFICIAL EFFECTS OF CYCLOHEXYL SUBSTITUENT ON THE IN VITRO ANTICANCER ACTIVITY OF DIIRON VINYLIMINIUM COMPLEXES

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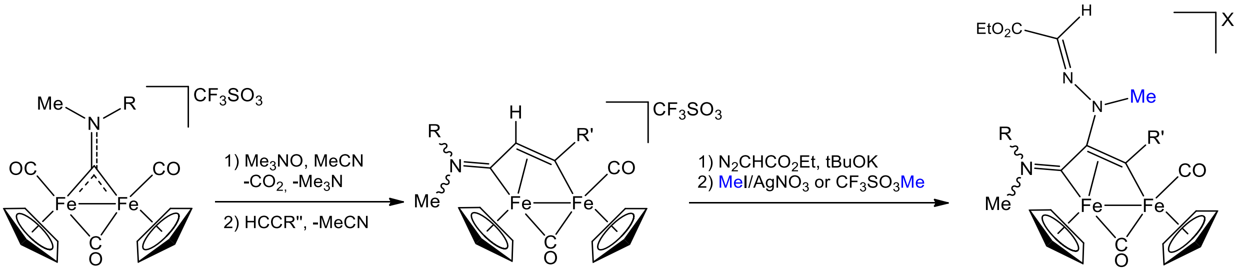
Diiron bis-cyclopentadienyl complexes with different bridging hydrocarbyl ligands have recently emerged as anticancer drug candidates[1-3]. Here, novel diiron vinyliminium complexes (**1**) were synthesized in good to high yields by alkyne insertion reaction from the parent diiron aminocarbyne complexes. Further, the reactions of selected products, **1**, with ethyldiazoacetate in the presence of a base, followed by *N*-methylation, afforded the hydrazone-vinyliminiumderivatives **2** (Fig. 1). The series of compounds **1** and **2** were characterized by analytical and spectroscopic techniques, and by single crystal X-ray diffraction in three cases. Complexes **1-2** display a satisfying water solubility and are inert in aqueous media; their antiproliferative activity was assessed on CT26 and U87 cancer cell lines, and the non-cancerousRPE-1 cell line. Some complexes of type **1**, bearing R' = cyclohexyl, stand out for their performance and selectivity towards cancer cells. The possible modes of action will be discussed.



1 **2**

Figure 1: *Synthesis of diiron vinyliminium complexes (**1**) via coupling of bridging aminocarbyne ligands with terminal alkynes (R = Me, R’ = 4-C_6H_4OMe, Cy, CH_2Ph, Me or Bn; R’’’= Cy, CH_2Cy, 4-C_6H_4OMe or Ph; X = NO_3, CF_3SO_3; Bn = benzyl, Cy = cyclohexyl) followed by addition of ethyl diazoacetate and subsequent methylation to hydrazone-vinyliminium complexes (**2**).*

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P8

FENTON LIKE REACTION USING Cu^I AS EFFICIENT CATALYST IN THE PRESENCE OF HYDROGEN PEROXIDE

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The present work highlights the formation of $OH^{\cdot}$ on the treatment of peroxide with Cu^I complexes. The generated $OH^{\cdot}$ then oxidizes DMSO via Fenton like process. This results in the selective conversion of DMSO generating methane and ethane. The Cu^I complexes were synthesized in the absence of oxygen using appropriate quantities of copper sulphate and ammonia. Further, the kinetics for the generation of $OH^{\cdot}$ were determined by the reaction of $H_2O_2$with the synthesized Cu^I complex by varying both peroxide as well as catalyst concentrations. This was followed by the reaction of H_2O_2 and Cu^I complex with the excess of DMSO and the products obtained were determined using NMR and Gas chromatography. The results obtained give an insight on high rates of formation of $OH^{\cdot}$ and efficient conversion of DMSO under environmentally friendly conditions.

P9

SILVER AND GOLD BISCARBENES SHOWED HIGH CYTOTOXIC ACTIVITY. SYNTHESIS AND IN SOLUTION STUDIES ON THE BINDING TO DIFFERENT BIOSUBSTRATES

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Auranofin (AF), introduced in 1985 for the clinical treatment of rheumatoid arthritis, was found cytotoxic against some selected cancer cell lines.[1]Since then, extensive studies have explored the possible applications of gold complexes as anticancer agents.[2] N-heterocyclic carbenes (NHCs) ligands turned out of particular interest for medicinally relevant gold complexes.[3] Also, Ag(I)-NHCs have been tested and showed an antitumor activity comparable to and, in some cases, higher than that of Au(I)-NHCs.[4] We will first describe some recent results on the activity of the Ag(I)-NHC-anthracenyl butyl imidazole bis-carbene fluorescent complex shown in Figure 1.

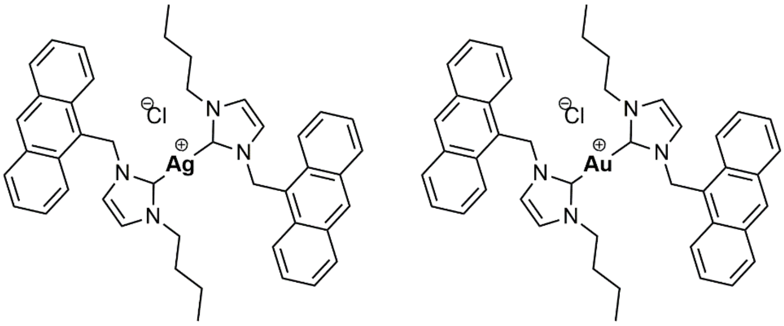

Figure 1. *Molecular structure of the 1-anthracenyl-3-butyl functionalized Ag(I)/Au(I) NHC bis-carbenes*.

We analysed the mechanistic details of its interaction with relevant biosubstrates such as duplex DNA, RNA, DNA G-quadruplexes (G4s), i-motif and serum albumin. To this aim, we did spectrophotometric and spectrofluorometric titrations, melting experiments, viscometric tests, FRET melting assays and gel electrophoresis experiments. The Ag(I)-NHC complex selectively interacts with DNA and not with RNAs and differently binds to G4s depending on their hybrid/parallel/antiparallel geometry. The solubility of the Au(I)-NHC is lower and prevents some experiments. However, some data on the gold counterpart enable us to discuss the different reactivity of the metal centres. Regarding their anticancer potential, MTT assays let us observe a high cytotoxic activity towards selected cancer cell lines.

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P10

(METAL CONTAINING) POLYHEDRAL SILSESQUIOXANES: A BRIDGE BETWEEN INORGANIC MOLECULES AND MATERIALS

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Polyhedral oligomeric silsesquioxanes (POSS) are a class of condensed three-dimensional oligomeric organosiliceous compounds with the cage framework having different geometries and symmetries. As a general feature, the molecular structure of these compounds consists of silicon atoms bonded to one- and-a-half oxygen (‘‘sesqui-’’) and hydrocarbon (‘‘-ane’’) moieties (herein denoted as R), leading to ($RSiO_{1.5}$) bond units.

They are called smart hybrid materials, with features of both molecules and siliceous materials, as well as inorganic and organic compounds, giving a relevant perspective, for nanoscience, to design and reproducibly tailor specific functional features.

Besides fully condensed polyhedral silsesquioxanes, with a cubic $R_8Si_8O_{12}$structure[1], open-corner POSS compounds, where a Si vertex missing giving a general formula $R_7Si_7O_9(OH)_3$, show the capability to link different functionalities through the reaction with specific organosilanes and heteroelement precursors allowing the preparation and use of multifunctional nanomaterials[2].

M-POSS can be prepared using corner capping reaction in solution, employing mild conditions and short times of reactions[3]. This allows to control of the final structure of the M-POSS, sincemonomer-dimer equilibria can occur. Lanthanide-containing POSS (Ln-POSS) can also be prepared, bridging luminescent features of this ion with a high thermal and mechanical stability.

A synthetic method led to obtain Ti, V, Al, Eu-POSS derivatives, explored for their properties for fire retardancy of polymers and catalysis.[4-5]

As Lanthanides, Eu^{3+} was successfully included: the metal ion caps the POSS unit via the open corner and expands its coordination with solvent molecules.

Eu(III)-POSS has proved a quantum efficiency of ca. 14%, and high photostability to photobleaching. [6]

Thanks to their molecular and hybrid nature, POSS and M-POSS are suitable for the dispersion in organic environment as polymers.

Application of these materials in polymer-based nanocomposites highlight their potential as functional additives operating at nanoscale level. Examples on the application of POSS in PVC[6] systems, and M-POSS in PP matrices[4] will be given.

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P11

POLYIMIDAZOLE LIGANDS: BIOLOGICAL ACTIVITY OF THEIR COPPER COMPLEXES

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Polypyridine ligands have been widely studied for their application in biological systems.[1] These chelators can form metal complexes with zinc, copper and iron showing the selectivity of antiproliferative activity in colon cancer cells. [2]

We recently synthesized polyimidazole ligands and we studied them as inhibitors of Metallo Beta Lactamases. [3]

Here we report a study about the cytotoxicity of polyimidazole ligands N,N′-bis((imidazol-4-yl)methyl)-ethylenediamine BISIM, N,N,N′-tris((imidazol-4-yl)methyl)-ethylenediamine TRISIM, and N,N,N,N′-tetra((imidazol-4-yl-methyl)-ethylenediamine TETRAIM and their copper(II) complexes.

In particular, we investigated the antiproliferative activity of the three ligands alone and in the presence of copper (II) towards three human cancer cell lines, K562 (chronic myeloid leukemia), CaCo-2 (colorectal adenocarcinoma), SH-SY5Y (neuroblastoma) and a normal keratinocyte line, HaCat cells.

Cells were exposed to increasing concentrations (from 6.25 to 100 µM) of compounds for 48 h, in the presence or absence of 20 µM $CuCl_2$.

A significant cytotoxic effect was observed only on K562 cells treated with 50 and 100 µM TETRAIM in the absence of $CuCl_2$. To better clarify the mechanism of antiproliferative activity induced by TETRAIM in K562 cells, we investigated apoptotic markers. It was observed about 33% and 60% of apoptotic cells after 48 h of treatment with 50 and 100 µM TETRAIM, respectively.

These results indicate that the inhibition of K562 cell proliferation, induced by TETRAIM, is associated with the activation of the apoptotic pathway. Moreover, the apoptotic activity of TETRAIM on K562 cells seems to be related to its chelating properties, since the addition of Cu^{2+} ions reverses the effect.

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UPCYCLING METHODS FOR ELECTRIC ARC FURNACE SLAGS: P-REMOVAL FROM WASTEWATER AND FILLERS FOR POLYMERS

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Electric Arc Furnace steelmaking slags (EAF-slags) represent one of the most challenging materials concerning their upcycling possibilities, because of their heterogeneous composition due to the presence of different metal oxides (e.g., FeO, Ca_2SiO_4, Mg_2SiO_4, $Ca_{12}Al_{14}O_{33}$). The present study is focused on the utilization of EAF-slags both as material for P-removal from wastewater[1] and as fillers for polymers[2], in order to investigate: i) their maximum P-sorption capacity and the possibility of P-recover and ii) the mechanical properties of polymeric matrices loaded with different weight percentages of EAF-slags. Regarding the phosphorus removal, different aqueous solutions with different concentrations of phosphorus were prepared, using KH_2PO_4 as precursor, and the adsorption kinetic was investigated by withdrawing a certain volume of the suspension at fixed times. UV-vis was employed for the detection of phosphorus (standard BS EN UNI 6878:2004). Concerning the polymers, the tested polymeric matrices were polypropylene and polymethylmethacrylate (PP and PMMA), and the slags (average particle size of around 20 μm) were added following two different routes: a) by synthesising the polymer and mixing EAF-slag through an extrusion step, and b) by functionalising the slags with different carboxylic acids (e.g., acrylic acid, methacrylic acid) being well-known the high affinity between carboxylic groups and metal oxides, before their mixing with the monomer solution and subsequent free radical polymerization, having all a polymerizable C=C moiety. Different EAF-slags weight percentages were employed (1 %wt., 5 %wt. and 10 %wt.) for the preparation of the samples and through tensile and flexural tests the final mechanical properties were investigated (i.e., tensile strength, elastic modulus, break at load).

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P13

MASTERING THE LnDOTA SERIES: MAGNETIC ANISOTROPY AND BOND NATURE UNDER THE LENS OF *AB INITIO* CALCULATIONS

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The [LnDOTA(H_2O)] family[1] (H_4DOTA = tetraazacyclododecane-N,N′,N″,N‴-tetraacetic acid and Ln = Ce-Yb) is a class of compounds of paramount importance in several research and technological areas, particularly in the fields of magnetic resonance imaging and molecular magnetism.[1] The computational and experimental investigation on this archetypal series allowed us to shed light on the electronic structure of lanthanide ions, to unveil its effects on magnetic anisotropy and finally to investigate the real nature of lanthanide coordination bond.

In this regard DyDOTA has been deeply investigated *ab initio* because of the crucial role of the apical water molecule in determining the magnetic easy axis orientation.[1,2] Our results on this complex have shown for the first time that a clear and crucial covalent footprint is present,[2] and for the same system the possibility of controlling the orientation of the magnetic axes as a function of pressure was demonstrated *in silico*.[3]

Grounded on the developed protocol, our combined experimental and computational study on the full LnDOTA series[4] revealed a new trend never observed before: the same alignment of the magnetic anisotropy tensors for Ln^{3+} ions differing by seven f electrons., that we named "the f^{n+7} rule".[4] This is a direct consequence of the 4f orbital occupation which is dictated by the competition of the Aufbau principle and Hund's rules.

Finally, we have experimentally evaluated its effect by successfully removing the water from the coordination sphere without altering the structure of the ligand.[5] As it was theoretically predicted, the results confirmed the apical water molecule as the key ligand in modulating the anisotropy of these complexes.

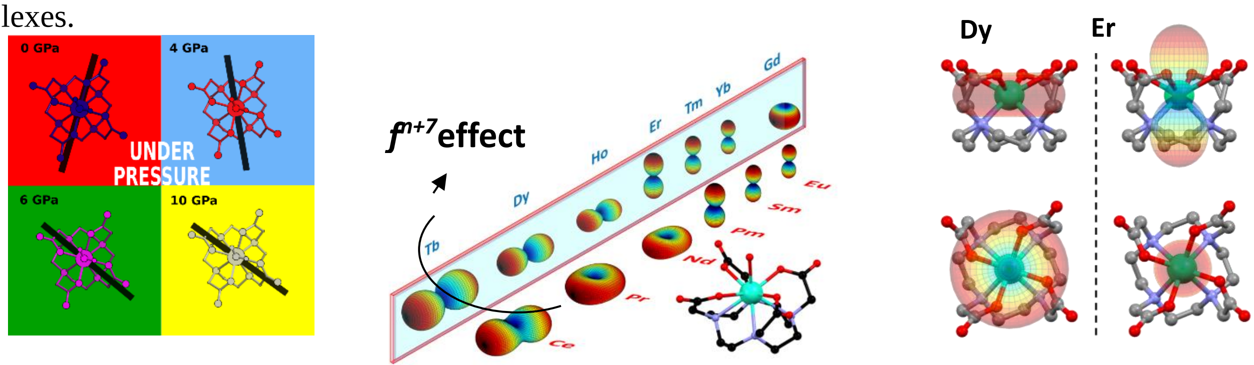

Figure 1*: (Left) [DyDOTA(H_2O)] easy axis'orientation as a function of pressure. (Center)The magnetic anisotropy of [LnDOTA(H_2O)] series. (Right)Magnetic susceptibility for DyDOTA and ErDOTA without apical water ligand*

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P14

SYNTHESIS OF RUTHENIUM(II) COMPLEXES BEARING BIS-NHC LIGANDS

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Noyori's ruthenium (II) hydrogenation and transfer hydrogenation catalysts are outstanding in the selective reduction of polar bonds, and complexes based on bis-phosphinic and arene ligands are among the most effective[1-2]. The high reactivity of these species in this class of reactions is ascribed to amino, bipyridine, and amino-pyridine type ligands also coordinated to the metal, which dictate the reaction mechanism followed by the catalyst[3]. N-heterocyclic carbenes (NHC) are regarded to possess stronger σ-donor properties and improved stability compared to phosphine ligands[4]. Interestingly, few examples of complexes bearing bis-NHC ligands are available in the literature with application to hydrogen borrowing reactions[5]. To fill this vacancy, we recently developed a new synthetic protocol for synthesizing ruthenium(II) complexes with a bis-NHC ligand and a broad scope of commercially available ligands (***Figure 1***). These new catalysts are currently being tested for the transfer hydrogenation, the hydrogenation, and the aerobic oxidation of organic compounds.

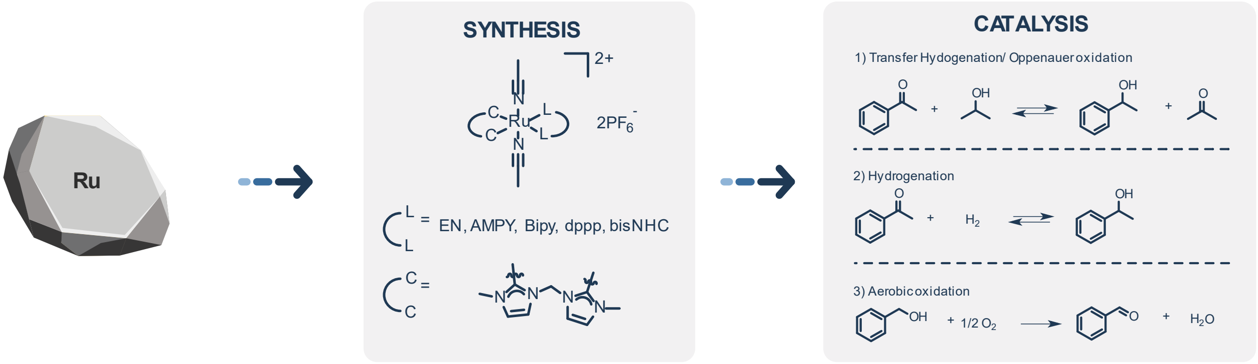

Figure 1*: Flow chart highlighting the synthesis of ruthenium(II) bis-NHC complexes from ruthenium(II) precursors and their application in catalytic reactions.*

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P15

MEDICINAL METAL IONS COMPLEXATION BY PHOSPHONATE CHELATOR

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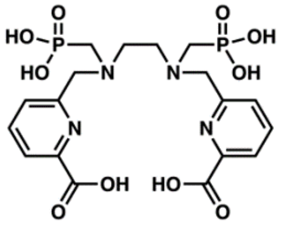
Phosphonate-bearing chelators have seen continued interest over recent years due to their well-known *hard* coordination electronics as well as their rapid kinetics of complexation. They are particularly well-suited toward the coordination of hard metal ions, such as transition metals as well as the entire lanthanide series. Picolinic acids are another motif commonly found in modern chelators. Among bifunctional chelators (BFCs), key components of contemporary metallo−radiopharmaceuticals, we present phosponate-picolinic acid ligand named H_6phospa (Figure 1). The ligand was fully characterized including X-raycrystallographic structures. Solution studies were carried out by potentiometry, UV and NMR spectroscopy to evaluate the complex stability towards trivalent metal ions such asSc^{3+}, Y^{3+}, In^{3+}, La^{3+}, Lu^{3+}. Formation constants were also calculated from DFT results using potential-energy optimized structures. Strong dependence of molecular free energies on explicit water molecule number, water molecule configuration, and protonation state was observed, highlighting the need for dynamic data in accurate first-principles calculations of metal−ligand stability constants. [1]



H_6phospa

***Figure 1**: Phosphonate-bearing chelator, H_6phospa*

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P16

INULIN COATED ZnO NANOPARTICLES FOR PRIMING OF *V. FABA*: SYNTHESIS, CHARACTERIZATION AND GROWTH OF SEEDLINGS

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Nanoparticles (NPs) are possible tools to release micronutrients in soils, control plant pests and diseases, recover soils from contamination, and promote plant growth. The achievement NPs tailored for agricultural purposes would help fulfilling the “Zero Hunger” sustainable development goals of the United Nations 2030 Agenda[1]. Recently, ZnO-NPs have gained interest in plant science as new fertilizers [2] and they are considered a solid solution to the problem of soil Zn deficiency[3]. Within this framework, we carried out the synthesis of ZnO-NPs and their functionalization with inulin, a disaccharide with biomimetic functions (Inu@ZnO-NPs), according to fully green purposely implemented protocols[4]. Subsequent characterization of the synthesized sample was conducted, employing several spectroscopic and microscopic techniques, including XRD, IR, TGA, SEM, EDX. Inu@ZnO-NPs were ensuingly dosed in soil and *Vicia faba* L. seeds planted. Further investigations were performed to check the bioavailability of the Zn in the cultivated plants. The stimulant property of Inu@ZnO-NPs on germination and growth of *V. faba* seeds and seedlings were examined, and the cellular and molecular effects of the NPs on plant tissues were determined. Moreover, content of photosynthetic pigments, genotoxicity, viability, induction of oxidative stress, generation of tissue damage, and antioxidant response were observed. The appraisal of all monitored parameters points at a beneficial effect of Inu@ZnO-NPs on *v. faba* growth. Finally, in order to gain a complete overview of the processes going on in primed soil, the role of the inulin as capping agent was determined.

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P17

COPPER COMPLEXES OF BIS(PYRAZOLYL)ACETATES CONJUGATED WITH BIOLOGICALLY ACTIVE MOLECULES AS POTENTIAL ANTICANCER AND ANTIVIRAL AGENTS

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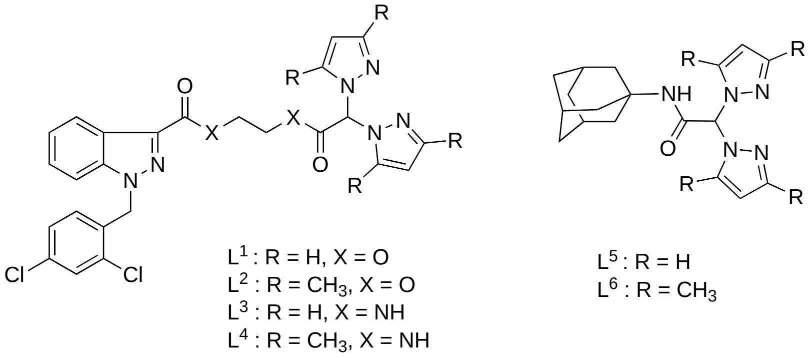
Copper complexes show broader spectra of activities and lower toxicity, thereby providing the possibility of circumventing the problems encountered by platinum drugs, such as dose-limiting toxicity and inherent/acquired resistance [1]. We have recently reported copper complexes with heteroscorpionate ligands conjugated with the derivatives of the antineoplastic drug lonidamine (L^1-L^4, Fig. 1), endowed with cytotoxic activity toward a panel of human tumor cell lines [2]. Here we describe the synthesis and biological evaluation of new Cu(I) and Cu(II) complexes functionalized with the antiviral agent amantadine (L^5 and L^6, Fig. 1). The bis(pyrazol-1-yl)acetic acids were selected as bifunctionalizable coordinating agents for the synthesis of the ligands due to the presence of a carboxylic function suitable for the coupling with primary amine groups. All the complexes with amantadine-conjugated ligands were primarily evaluated for their cytotoxicity on two mammalian immortalized cell lines, such as HaCaT and Vero E6 cells, by MTT cell viability assay. The results highlighted that all the Cu(II) complexes and the Cu(I)-PTA complexes showed good biocompatibility profiles at both the studied cell lines and have been selected to be tested in vitro for their antiviral activity by using lentiviral vectors expressing luciferase in Vero E6 cells.



L^1 : R = H, X = O
L^2 : R = CH_3, X = O
L^3 : R = H, X = NH
L^4 : R = CH_3, X = NH

L^5 : R = H
L^6 : R = CH_3

***Figure 1**: Structures of bis(pyrazolyl)acetate conjugated ligands*

***Acknowledgements**: Next GenerationEU - D.M. 737/2021 "INVIRCuM" University of Camerino FAR 2022 PNR*

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P18

NEW CHEMICAL INSIGHTS INTO THE ACTIVATION MECHANISM OF THE TELLURIUM PRODRUG AS101: TOWARDS A BETTER UNDERSTANDING

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Metalloids -even known as semimetals- though only sporadically investigated, offer a rich and peculiar chemistry for their use in the preparation of compounds endowed with remarkable medicinal properties.Among metalloid-based drugs, several Tellurium derivatives, both organic and inorganic, present a really promising biological activity, due to their redox chemistry, and ability to interact with biomolecules such as cysteine- and selenocysteine- residues of proteins and enzymes.[1] In particular, AS101 (Ammonium trichloro (dioxoethylene-O,O') tellurate) (*Figure 1*) is an important hypervalent Te-based prodrug. Interestingly, to date, a few papers report on the activation mechanisms and a substantial agreement on the rapid conversion of the initial species AS101 into the corresponding $[TeOCl_3]^-$ anion do exist [2]; this latter species being reputed the pharmacologically active one. However, we realized as $[TeOCl_3]^-$ could quickly undergo further steps of conversion in water media, eventually producing the TeO_2 species. Spurred by the curiosity for this observation, we started investigating in more details the process. Here, using a mixed experimental and theoretical investigation approach, we tried to characterize the conversion process leading from $[TeOCl_3]^-$ to TeO_2, discussing chemical, mechanistic, and biological implications.

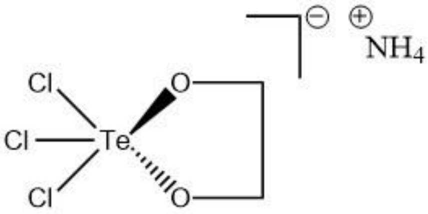

***Figure 1**: Chemical structure of AS101.*

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P19

BORON SPIRO-COMPOUNDS WITH IMIDAZO[1,5-*a*]PYRIDINE LIGANDS

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Imidazo[1,5-*a*]pyridine ligands have garnered significant attention due to their intriguing photochemical and biological properties.[1, 2, 3, 4] Typically, these molecules can act as neutral N,N-bidentate ligands; however, recent literature has proposed an alternative approach by employing them as N,O-coordinating ligands,[5] overcoming the dissociation issues associated with N,N- bound systems. Herein, we present our latest findings on the synthesis and characterization of boron compounds obtained by reacting 9-chloro-9-borafluorene with a N,O-imidazo[1,5-a]pyridine phenol. The incorporation of boron into the imidazo[1,5-*a*]pyridine ligand imposes a certain rigidity on the structure, thus leading to a noticeable increase in the luminescence properties compared to the free ligand. The structure of the compound was also resolved by X-ray analysis, revealing a spiro arrangement generated by the imidazo[1,5-a]pyridine and the fluorene fragments. It was possible to obtain two different polymorphs which have shown different luminescence properties.

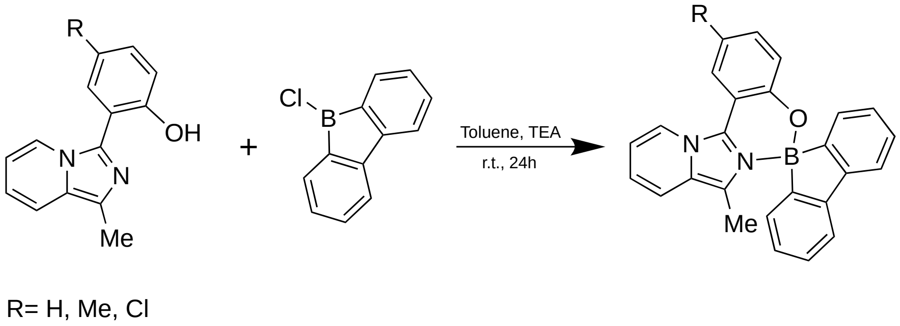

Figure 1*: synthesis of the SPIRO compound.*

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P20

ELECTRO TRIGGERED SELF ASSEMBLY OF METAL PHENOLIC NETWORKS

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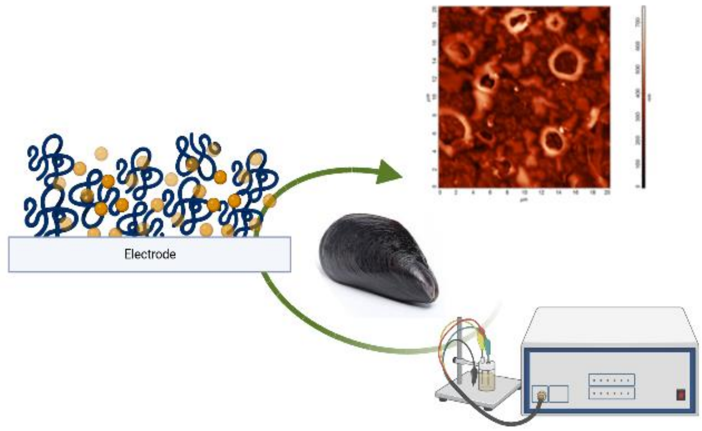

Figure 1. *Schematic representation of mussel inspired adhesive materials obtained by electrodeposition*

Nature is a great source of inspiration by virtue of millions of engineered and crafted processes and materials. Inspired by Nature, a new class of biomaterials is emerging: metal-phenolic networks (MPNs).[1-2]They are hybrid materials, i.e. constituted by an organic (polyphenols) and an inorganic (metal ions) part. MPNs have interesting adhesion capacity, dependent on catechol chemistry, that makes them eligible for surface coating.[3] Indeed, like catechol chemistry seems to govern the adhesion of mussels to marine rocks, MPNs may represent an intriguing advancement in the search of engineered nanomaterials with tunable adhesion properties. [4,5] An appropriate choice of polyphenol or metal ion allows to tune the physicochemical properties of the resulting material. In this holistic approach, electro triggered self-assembly strategy represents a Nature-inspired process to obtain new materials. The electrochemical manufacturing strategy is tested on a group of catechol-based molecules, with natural origin or properly synthesized, in presence of Fe(III) ions. The resulting supramolecular network was characterized by means of AFM, SEM, EDX and UV-vis. The AFM analysis will be deeply discussed and the observed surface morphology will be correlated to the film growth mechanism.

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P21

LATE-TRANSITION ANTICANCER METAL COMPLEXES WITH N-HETEROCYCLIC CARBENES AND PEPTIDES COORDINATED: SYNERGY BETWEEN TWO WORLDS

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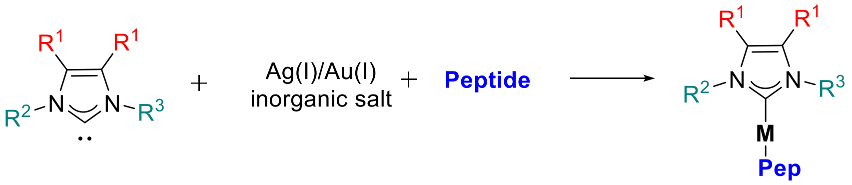
The improvement of drug bioavailability and the lowering of potential side-effects are among the most crucial challenges in cancer therapy. Such benefits can be ensured by tumour-targeting drug co-assemblies; metal drugs conjugation to cell-penetrating peptides increases cell membrane crossing and specificity.[1] Metal complexes' therapeutic efficiency lies in their structural variety, granted by multiple coordination numbers and geometries, as well as redox properties.[2] Coinage metal complexes have been considered as valid alternatives to the classical drugs, thanks to improved cytotoxicity.[2a] N-heterocyclic (NHC) carbene complexes display remarkable bioactivity, mainly due to the carbonaceous backbone, which bestows high biochemical stability.[3] In this contribution, we propose an innovative drug design approach meant to unite NHC metal complexes' therapeutic potential with peptides' bioselectivity, furnishing an extended library of co-assembled NHC complexes bearing an oligopeptidic counterion. Systematic modulation of the steric and electronic characteristics of substituents on the backbone (R^1) and/or at nitrogen atoms (R^2, R^3) of the ligand will be described (Figure 1), together with the design of specific oligopeptide counterions. The experimental results, stated by the investigated anticancer activity on several cancer cell lines, together with molecular modelling, demonstrate the enormous pharmacological potential of these co-assembled organometallic compounds, combining bioinorganic and peptide chemistry.



M = Au(I), Ag(I)
Pep = amino acid or oligopeptide
R^1 = hydrogen, halogen, aryl
R^2, R^3 = hydrophylic moieties

***Figure 1**: Co-assembled N-heterocyclic carbene – peptide metal complexes.*

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P22

LIGHT TRIGGERED HYDROGEN EVOLUTION PROMOTED BY NOVEL RUTHENIUM-BASED PHOTOSENSITIZIER

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In the last few years, light-driven processes have gained significant attention as a promising approach for harnessing solar energy. In particular, harnessing the hydrogen evolution reaction (HER) to produce carbon-free fuel hydrogen has captured widespread interest [1]. An efficient and cost-effective method for hydrogen production, *via* light-driven water splitting, involves combining a photosensitizer and an electron donor with redox-active metalloenzymes under mild conditions [2]. Among different types of photosensitizers, ruthenium polypyridyl-based complexes (RuPOP) feature: (i) intense UV-Vis absorption, (ii) stable and long-lived triplet states, (iii) versatile photophysical properties, tunable by modifying the ligands [3]. In this work, a heteroleptic ruthenium(II) complex with two bipyridine moieties and one phenantroline-based ligand (RuAPPO) was synthesized and a protocol for the purification of the crude mixture was developed. To achieve the required purity for physico-chemical characterization, a combination of size exclusion chromatography and reversed-phase flash chromatography was performed. The resulting pure product was then characterized by UV-Vis spectroscopy and mass spectrometry. Finally, RuAPPO was tested for photosensitized electron transfer to a bioinspired HER catalyst. The latter, a cobalt derivative of MimochromeVIa (CoMC6a), is a rationally designed porphyrin-peptide conjugate that has demonstrated remarkable catalytic activity, longevity, and stability for electrochemical and photoinduced HER under mild conditions [4,5]. Our results show that RuAPPO is able to reduce Co(III)MC6*a in anhydrous DMF only when the sacrificial electron-donor (triethylamine, TEA) was present and blue light irradiation (447 nm) was applied. Further, analysis in aqueous solution and kinetic studies are being performed to investigate the mechanism of the photo-induced electron transfer (PET) activity.

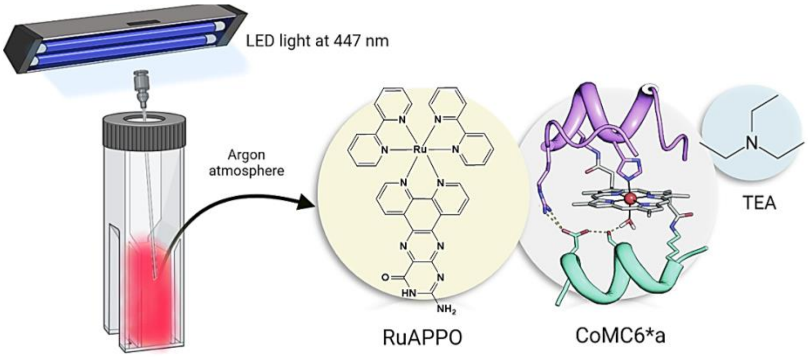

***Figure 1**: Schematic representation of photo-reduction of CoMC6*a with RuAPPO and TEA using LED light.*

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P23

EPR SPECTROSCOPY AS AN UNCONVENTIONALTOOL FOR MONITORING THE EXSOLUTION PROCESS IN Cu-DOPED SrTiO$_3$

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Supported nanoparticle systems have received increased attention over the last decades because of their potential for high activity levels in catalytic conversions though, due to their nanoscale nature, they tend to exhibit problems with long-term durability. Mostly in the frame of perovskite-type, the recent discovery of the so-called redox exsolution has addressed many of these challenges, providing a relatively simple, single-step, synthetic pathway to produce supported metal NPs combining high stability against agglomeration and poisoning, and superior catalytic properties [1]. This approach represents an "inside-out" route where the guest elements (e. g. Cu, Co, Ni ions), via usage of high temperature and low oxygen partial pressure, get reduced to elemental state and nucleate on the surface as NPs [2]. Since the process occurs under reducing conditions, by exposing the material to an oxidative atmosphere, the reaction can be reversed, and the metal NPs can be redissolved in the lattice [3]. The concentration, position, and type of defects in the matrix play an important role in the effectiveness of exsolution [4]. Therefore, the knowledge of defect chemistry of the oxide and redox behavior of metals are mandatory to understand and monitor the process.

In this context, the present work aims at the preparation and characterization of Cu-doped SrTiO$_3$ systems exploiting redox exsolution, with a special focus on monitoring, during the process, the evolution of the perovskite defectivity as well as the variation of metal oxidation state and coordination environment by Electron Spin Resonance (ESR). In detail, quasi-in-situ measurements have been carried out to monitor the modifications of the paramagnetic defects during the exsolution in terms of change in coordination and oxidation state of Cu^{2+} ions and as regards the generation/evolution/annihilation of O and Sr vacancies (V$_O$ and V$_{Sr}$) [5]. To this end, the sample has been heated up to 900° C under Ar/H$_2$ reducing atmosphere to promote the exsolution. The process was divided into several steps, at the end of which the sample was quenched at the temperature of liquid N$_2$ to "freeze" the process and the ESR spectra recorded at 130 K. Changes in the Cu^{2+} signal intensity has been retrieved as well as the formation of V$_O$, V$_{Sr}$ and Ti^{3+} species. Afterwards the reduced powders underwent re-oxidation in O$_2$ to assess the reversibility of the procedure and spectra were acquired. XPS, UV-DRS and HR-TEM analysis before and after exsolution were also performed to corroborate the modification of the defect structure. This work represents the beginning of a new way of monitoring the redox exsolution process in technologically relevant materials by using non complicated techniques.

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P24

SYNTHETIC MODELS OF NEUROMELANINS AND NITRATIVE STRESS

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Parkinson's disease (PD) is a neurodegenerative pathology related with mitochondrial dysfunction and oxidative and nitrative stress and characterized by progressive loss of dopaminergic neurons in *substantia nigra* (SN).[1] Despite the PD arising mechanism has not been fully clarified yet, it has been established that PD is associated to high levels of neuromelanins (NMs).[2] NMs are dark pigments with melanic, lipidic and peptide components linked together by covalent bonds, which accumulate during aging and exhibit both neuroprotective, since their synthesis prevent dopamine (DA) accumulation, and neurodegenerative effects.[2,3] As regards the NMs found in the SN, the melanic part is constituted by DA, which can be oxidized to quinone and then polymerize (Figure 1).[3]
Only a small amount of NM can be isolated from the human brain,[3] so it is very important to develop synthetic models of NM for research purposes. In this study, we prepare synthetic NMs from DA and β-lactoglobulin (BLG), a whey and milk protein of ruminants.[4] Moreover, in this study we take into consideration the nitrative stress, which is related to PD. In fact, under pathological conditions, nitric oxide (NO), a signaling molecule generated by nitric oxide synthase, can interact with reactive oxygen species (ROS) to generate reactive nitrogen species (RNS).[1]
The aim of this work is to investigate the effect of the nitration reaction in the presence of H_2O_2 and NO_2^-, either on the protein or the melanic portion of the synthetic NMs. First, our mass spectrometry data show that the nitration sites on BLG are tyrosines Tyr_{42} and Tyr_{99}, and that the nitration yield increases with the fibrillated protein, fBLG, since in its structure the tyrosines which undergo nitration are more solvent-exposed. Moreover, tyrosine nitration has been confirmed also in the protein treated with the H_2O_2/NO_2^- system after the melanization reaction, but it is to confirm whether the nitration occurs on the melanized protein or on the non-reacted portion. Then, since it was previously assessed that melanization reaction can't occur in presence of the only nitrated DA (6-nitrodopamine, 6-NDA), synthetic NM samples have been prepared with a DA/6-NDA mixture and analyzed by NMR spectroscopy. The protein peaks broadening in NMR spectra confirms the melanin formation; moreover, since these spectral modifications are more evident in the sample with BLG with respect to fBLG, we may hypothesize that either fBLG possesses a less tendency to melanize, or the melanization process with the fibrillated protein is faster but insoluble products, which cannot be seen in the NMR spectra, form.
As future perspective, this study could be completed by testing synthetic NM samples pre-nitrated on both the protein and the melanic portions.

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POTENTIOMETRIC AND ZETA POTENTIAL TITRATIONS FOR THE STUDY OF THIOL-PEG COATINGS ON GOLD NANOPARTICLES

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A precise characterization of the coating of inorganic nanoparticles is crucial for their stability as well as for successive modifications and in turn for the design of safe and efficient functional materials. In case of coating molecules presenting ionizable groups, the investigation of their protonation stateis key and potentiometric methods can help understanding how theiracid-base properties are affected when confined on the NP surface.[1]

Citrate-capped spherical AuNP have been coated with a series of α, ω bifunctional PEG of general formula $HS-(CH_2CH_2O)_n-CH_2COOH$ with different molecular weights ranging from few monomeric units to mw=5000.The number of molecules per particle has been determined by TGA, confirming a decrease of the number density with increasing length of the PEGchain.[2,3]

Preliminary potentiometric titrations have been performed on a series of HS-PEG, PEG-COOH and HS-PEG-COOH free molecules to determine their pK_avalues, finding a decrease of the acidity of the carboxylic acid with increasing length of the polymer chain. Then, to evaluate the effect of the binding on the NP surface, highly concentrated solutions of AuNP coated with HS-PEG$_{3000}$-COOH and HS-PEG$_{5000}$-COOH were titrated. In both cases, a shift of ca.1 log unit has been found for the apparent pK_a of the -COOH groups. This can be explained by the reduced tendencyofeachgroup to undergo deprotonation in presence of other nearby molecules grafted on the NP surface on which negative charges are building up during the course of the experiment.

To overcome the difficulties encountered with standard potentiometric titration, that requires a demanding procedure of purification and concentration to obtain suitable NP samples, zeta potential titrations have been carried out for comparison. This techniqueallows more practical measurements that directly reflects the protonation status around the NP. Fitted values of apparent pK_a show smaller shifts from the free molecules compared to those obtained by potentiometric titrations, while maintaining the trend of increasing acidity with decreasing PEG mw.

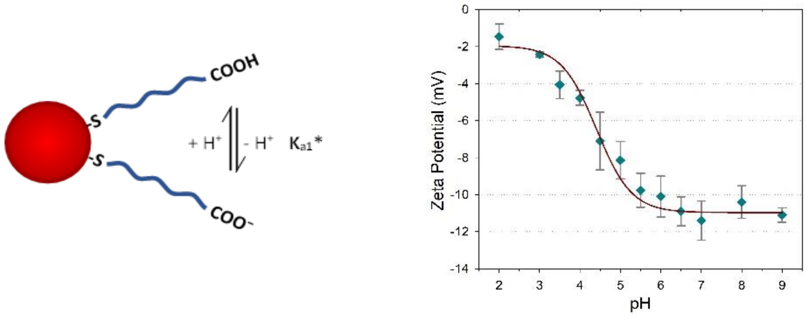

Figure 1: *(left) Protonation equilibrium of a generic HS-PEG-COOH molecule grafted on a spherical GNP surface; (right) Zeta potential titration curve for GNP coated with HS-PEG5000-COOH.*

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METAL COMPLEXES SUPPORTED BY STERICALLY HINDERED β-DIKETONATES DIFFERING IN THE PRESENCE OF FLUORINATED MOIETIES

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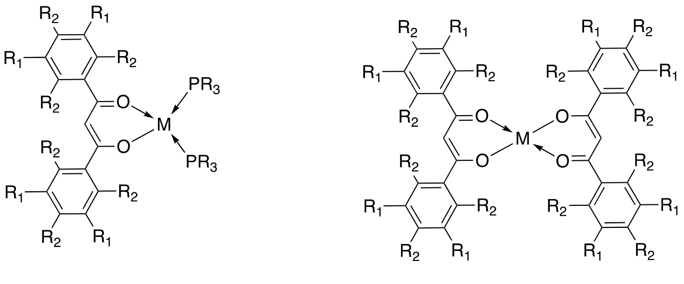
Although β-diketones represent one of the oldest classes of chelating ligands, their coordination chemistry continues to attract much interest, due to the ability of related metal complexes to support several unique and important catalytic reactions and for their applications as biochemically active agents. It is often noted that even modestly sterically hindered β-diketones offer improvements over the parent acetylacetone. β-diketones are known to form complexes with almost every metal, and they have been used as supporting ligands for metal-based anticancer agents[1]. In particular, the phenyl ring substituents increase the lipophilicity and improve cellular uptake, whereas the electron-withdrawing CF_3 groups can modulate the pharmacokinetic and physicochemical properties and the chemical reactivity of the resulting metal complexes[2]. Therefore, as part of our continuous investigation on the chemical and biological properties of metal-based coordination compounds[1],we report here a study on the syntheses, characterization, and biological evaluation of new homoleptic ($[ML_2]$; M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) and heteroleptic ($[ML(PR_3)_n]$; M = Cu(I) or Ag(I); PR_3 = PR_3 or PTA) metal-complexes supported by the anion of sterically hindered β-diketonate ligands, 1,3-dimesitylpropane-1,3-dione (HL^{Mes}) and 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one (HL^{CF3}). A particular attention was devoted to the synthesis of Cu(II) and Cu(I) species, also in view of their biological activity as potential antiviral and anticancer agents.



$R_1 = CF_3$; $R_2 = H$
$R_2 = CH_3$; $R_1 = H$
M = Cu or Ag
$PR_3 = PPh_3$ or PTA

M = Cu(II) or Zn(II)

***Figure 1**: Chemical structures of Cu(I), Ag(I), Cu(II) and Zn(II) complexes.*

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P27

Al-Zn-TM (TM = Hf, Zr) SYSTEMS: PHASE EQUILIBRIA AND EXPERIMENTAL DETERMINATION OF THERMODYNAMIC PROPERTIES

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Al-based alloys have a wide range of application ranging from materials for the automotive industry going through the aerospace application to structural materials [1]. Cubic $L1_2$ (cP4-$AuCu_3$) trialuminides have long been of interest because of their possible use as low density, high-temperature structural materials [2] and for their possible use as precipitates for high-temperature, creep-resistant Al-based alloys [3]. In this work we have investigated two ternary systems characterized by presence of a cubic $L1_2$ phase TM(Al,Zn)$_3$ (TM = Zr, Hf) showing a wide range of existence. Our focus was on the experimental measurement of the $\Delta_f H°$ at 300K by a calorimetric method [4] of the $L1_2$ cubic phase and about the determination of the phase equilibria at 600°C in the Al-rich side of the system (see figure 1). Composition and state of all investigated samples were carried out by means of Light Optical Microscopy, Scanning Electron Microscopy coupled with Energy-dispersive X-ray spectroscopy and X-ray Powder diffraction analysis.

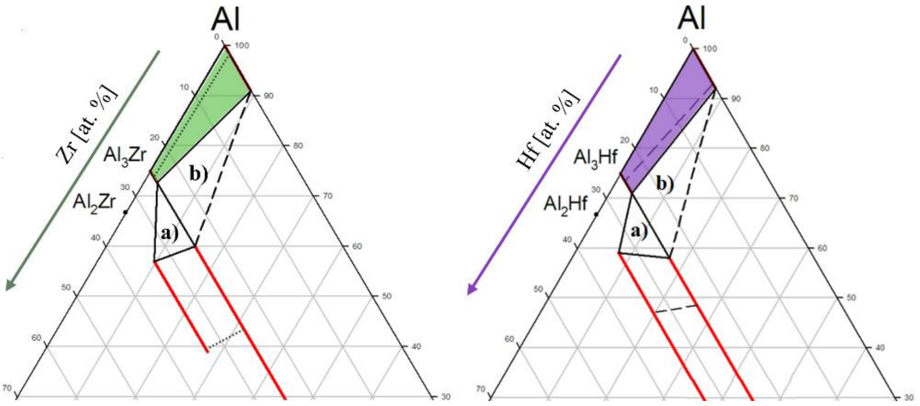

***Figure 1**: Hypotheses on phase equilibria at 600 °C [this work]*

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P28

ENCAPSULATION OF SNAIL SLIME IN METAL ORGANIC FRAMEWORK ZIF-8

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Zeolitic Imidazolate Framework, in particular *sod*-Zn(mIM)$_2$, also known as ZIF-8, has been widely established in the literature as a potential candidate for on-demand drug delivery applications, since it has a remarkable loading capacity, stability in physiological environments, and tunable drug release properties.[1-3]

As can be seen in *Figure 1*, in this work is investigated the encapsulation of snail slime extracted from *Helix aspersa muller* into the Zn(mIM)$_2$, for future biomedical applications.[4]For a comparison, also the pure absorption of snail slime on the surface of ZIF-8 has been investigated.

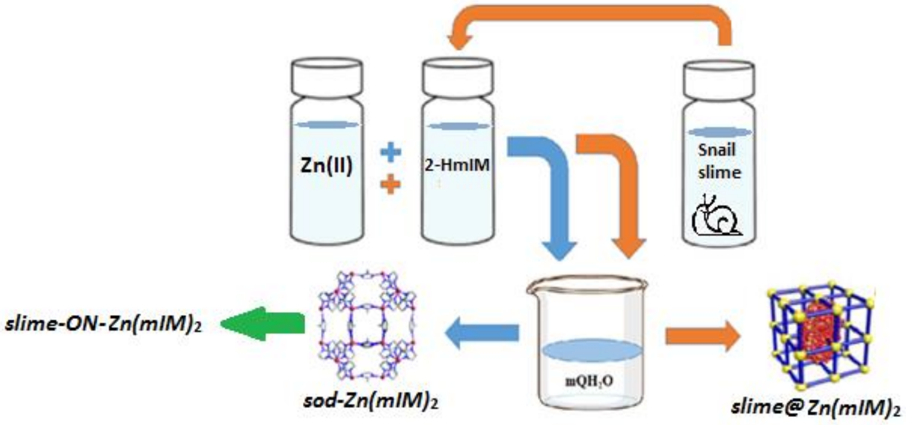

Figure 1: *Scheme of the synthesis of slime@Zn(mIM)$_2$ (orange path), Zn(mIM)$_2$ (blue path) and slime-ON-Zn(mIM)$_2$ (green path).*

Fluorescence Spectroscopy, SEM-TEM, ICP, TGA, XRD, FTIR, surface area and porosity analysis have been the main techniques that were used for a detailed characterization of the samples.[2, 3]

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P29

HYDROGEN AND HALOGEN BOND IN POLYHALIDE DABCO SALTS EXPLORED BY CRYSTALLINE VIBRATIONAL AND DFT INVESTIGATIONS.

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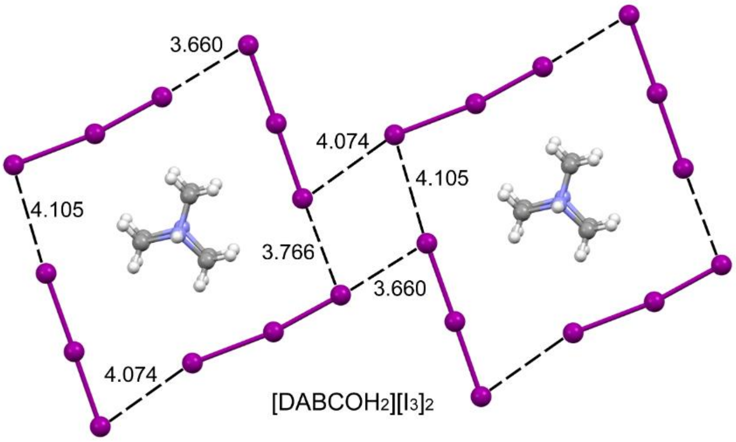

The strong intermolecular interactions of iodine make this species a good candidate for preparing compounds with interesting electronic properties, suitable for molecular materials employable in electronic devices, like pervoskite-based solar cells. X-ray structural studies and vibrational spectroscopies are good instruments to explore the intermolecular interactions responsible for the solid state architectures of iodine and polyiodide molecular solids, and their results may be integrated with an analysis of the topology of electron density obtained from a DFT modelling of the crystal structure. In this communication we report the preliminary results obtained from the investigation of as series of isostructural protonated DABCO salts with poly-halides, I_3^-, I_2Cl^- and I_2Br^-. The role of halogen bond and hydrogen bond to the organisation of the crystal structure have been explored by means of a vibrational analysis applied to the crystal structure and a force field has been obtained, in order to make explicit the contribution and change of intermolecular interactions with the differing anions.

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DEVELOPMENT AND CHARACTERIZATION OF INORGANIC MATERIALS AND THEIR APPLICATION IN ACTIVE PACKAGING

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Sliced and packed bread is a type of food that must have a long shelf-life. Preservatives are commonly included among the ingredients or added post-baking (i.e. ethanol) to avoid the formation of moulds. Nowadays consumers demand for healthy foods possibly without chemical preservatives that may change taste and smell of the product. However, eliminating preservatives would obviously result in a shorter shelf life and, consequently, in a increment in food waste. The study carried out aims to prepare inorganic active materials to include in packaging, that are able to extend the shelf life of food. For this application we considered clays and aluminum silicates that have the capability to improve the barrier and mechanical properties of film packaging and to slowly release antimicrobial ions, as Ag^+ and Cu^{2+}. Zeolites and Montmorillonites have been loaded with silver and copper cations and fully characterized (morphology, quantification of metals and ion release) [1]. Furthermore, the dimensions and shape of these materials, and the quantity of metals loaded and released have been checked to fulfill the limits allowed by EFSA directives [1,2]. After this study, the active materials have been embedded into biodegradable packaging formulations, both polysaccharides-based and polycaprolactone-based. These films were fully characterized as regards the effect of the inorganic materials on the mechanical properties, water vapor and gas permeability and morphology of the original films. [1,3] Shelf-life test of bread packed with our active films (fig. 1A) and release tests were carried out for compliance with EFSA and EU regulations (fig.1B) [1-3]. Then antimicrobial tests were performed, that assessed the effectiveness of the active materials.

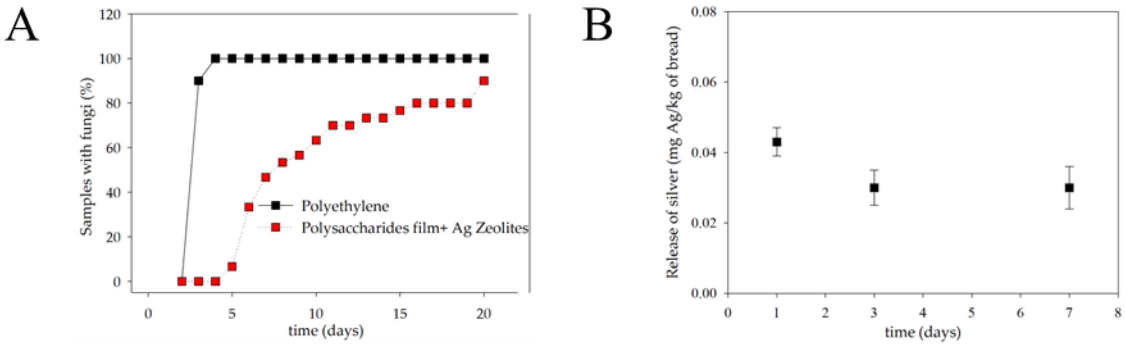

***Figure 1**: A) shelf life test of bread slices without preservatives; B) release of silver of polysaccharides films+AgZ.*

***Acknowledgements**: Millbosrl for granting, Alessandro Girella (Unipv) for SEM imaging.*

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CODING CROSS SECTIONS OF AN ELECTRON CHARGE TRANSFER PROCESS: ANALYSIS OF DIFFERENT CUTS FOR THE ENTRANCE AND EXIT POTENTIALS

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In this work we present the algorithm of a code written for exploring the collision dynamics of an electron transfer process between a neutral species and helium cation. Cuts of the entrance and exit potential energy surfaces are calculated in function of the radial distance to the center of mass of the neutral molecule, inclination angle and azimuth. Entrance and exit potential are calculated accounting for the electrostatic contribution and for non-electrostatic forces by employing the Improved Lennard-Jones function.
In this work, the results of a computational study on the reaction of destruction of one of the detected iCOM, methanol (CH_3OH), by collision with He•+ is presented[1]. The dissociative charge (electron) exchange mechanism has been obtained by computing the entrance and exit multidimensional Potential Energy Surfaces (PESs). For the reaction between methanol and He•+, the non-adiabatic transitions between the PESs have been modeled using an improved Landau-Zener-Stückelberg approach[2].

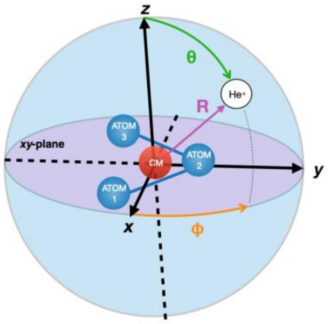

Figure 1*: Scheme representing a system in a three-dimensional space.*

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INVESTIGATION ON THE EMISSIVE PROPERTIES OF NCN-Pt(II) COMPLEXES UNDER VARIABLE TEMPERATURE AND PRESSURE

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Transition metal complexes represent useful tools to be exploited in different fields, thanks to the presence of the heavy metal center which allows for an efficient population of the triplet excited states, from which the emission of phosphorescence can occur in high quantum yields.

In particular, very high luminescence efficiencies are obtained with platinum(II) complexes bearing a terdentate chelating NCN-type ligand of the 1,3-di(2-pyridyl)benzene family (structure in Figure 1), leading to various applications, *e.g.* as dopants in OLED devices[1, 2] or as dyes in biological systems[3].

Some complexes belonging to this family, in which the benzene ring bears a mesityl moiety and the ancillary ligand on the metal is a chloride (Pt1, Figure 1), an isothiocyanate (Pt2) or a phenyltetrazole-thiolate (Pt3), have been studied for their photophysical properties and the results of the luminescence measurements will be presented, together with the synthetic pathway followed to obtain the complexes and with the X-ray crystal structure of the platinum compounds.

The measurements have been performed at the solid state under variable pressure and temperature, to find out which variations occur in the emission spectra under different conditions.

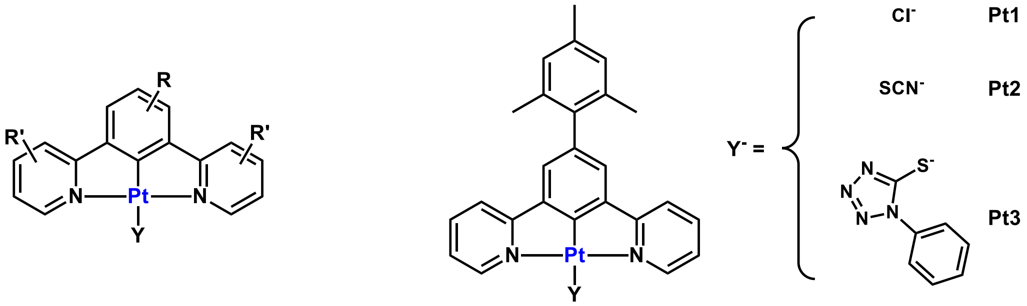

***Figure 1**: General structure of the NCN-Pt(II) complexes and of compounds **Pt1-Pt3**.*

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P33

^{1}H-NMR BASED METABOLOMICS ASSESSMENT OF METAL IONS BIOCOMPLEX ENDO-THERAPY TREATMENT IN *Xylella fastidiosa* INFECTED OLIVE TREES

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Over the last decade, a severe threat caused by *Xylella fastidiosa* subsp. *pauca*, affected the Salento olive groves (Apulia, South-East Italy). Very few phyto-therapeutics, including a Zn/Cu citric acid biocomplex foliar treatment, were successfully evaluated [1-2]. Recently, we performed, a short-term monitoring of metabolic pathways reprogramming for infected olive trees after precision intravascular biocomplex delivery [3]. The ^{1}H NMR-based metabolomics approach showed specific changes in the content of some metabolites such as a decrease of both quinic acid and mannitol with increase of oleuropein related compounds. Analytical information showed as both the zinc and copper ions reached the tree leaves buttressing the correlation of the observed metabolic changes with the therapeutic treatment, Figure 1.

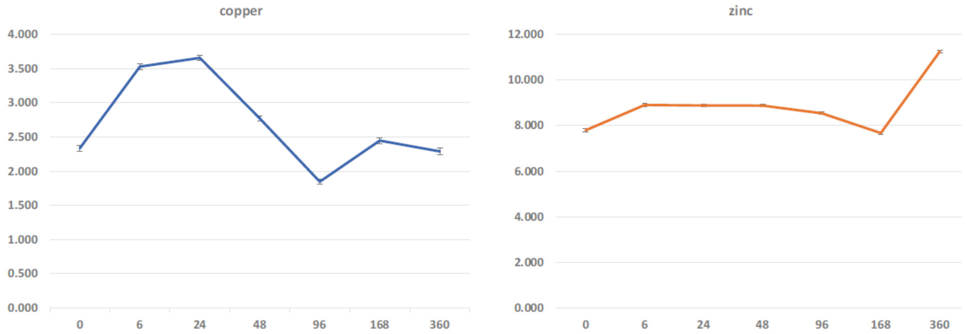

Figure 1. *Time course of copper and zinc leaf concentrations at 0, 6, 24, 48, 96, 168, and 360 hours after Cu/Zn biocomplex injection. The elements' average concentrations are expressed as ppm (mg/kg of fresh weight)* [3].

Medium-term effects of different doses of agro-active endo-therapy treatments in comparison with traditional foliar application were also evaluated [4]. The comparisons of ^{1}H NMR-based metabolic profiles suggest the need for further doses/frequencies trimming to obtain long-term results besides a possible more effective performance of endo-therapy with respect to foliar treatments. The present studies on *X. fastidiosa* control disease offer an example of useful NMR metabolomics application for plant monitoring under metal ions-based drugs therapy.

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P34

MATERIAL SCREENING BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR BACKROUND CHARACTERIZATION IN RARE EVENTS SEARCH EXPERIMENT AT GRAN SASSO NATIONAL LABORATORIES

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Astroparticle physics experiments need an environment with very low contamination level to reach high sensitivity, these are important required factor to observe signals of rare events; following this approach, underground laboratories are an ideal location to host these experiments. Gran Sasso National Laboratory (LNGS) is largest underground laboratory in all over the world, overbunden rock is able to shield cosmic ray flux by one million times, also neutron flux is about thousand times less from external environment due to rock composition with very low amount of thorium and uranium. Several experiments related to astroparticle physics are placed at LNGS, specially experiments related to neutrinos and dark matter, also underground biology experiments are located in underground laboratory[1].

Principal purpose of this experiments is to continuously achieve higher sensitivity, observation of rare events signals requires low background; several sources can affect background, as same materials due to them intrinsic radioactivity.

Among necessary requirements in this type of experiment, there’s achievement of higher sensitivities, in order to obtain a low background suitable for signals observation related to rare events. Regards to various contributions correlated to low background, materials have considerable importance as they have a natural intrinsic radioactivity to take under consideration for their eventual use[2].

Using of high pure materials is necessary to reach low background, during installation and maintenance of an experiment, several materials with different characteristics are utilised in experimental apparatus; a screening campaign to check impurities is fundamental to decree possible use of specific material or production batch for intended purpose.

Purification process is a possible way to apply on different type of materials to make them suitable for various applications, especially for physics experiments on rare events; a peculiar study focused on chemical treatments is important to choose and perform best process with maximum yield.

Different materials (plastic, metals, organic) can be characterized through ICP-MS analysis[3], different treatments were carried out to solubilize them; in fact, ICP-MS technique needs liquid solution to perform analysis, so an important step to study is related to mineralization of samples.

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P35

SHEDDING LIGHT ON PERSULFURATED BENZENES: HOW TO TUNE THEIR LUMINESCENCE PROPERTIES

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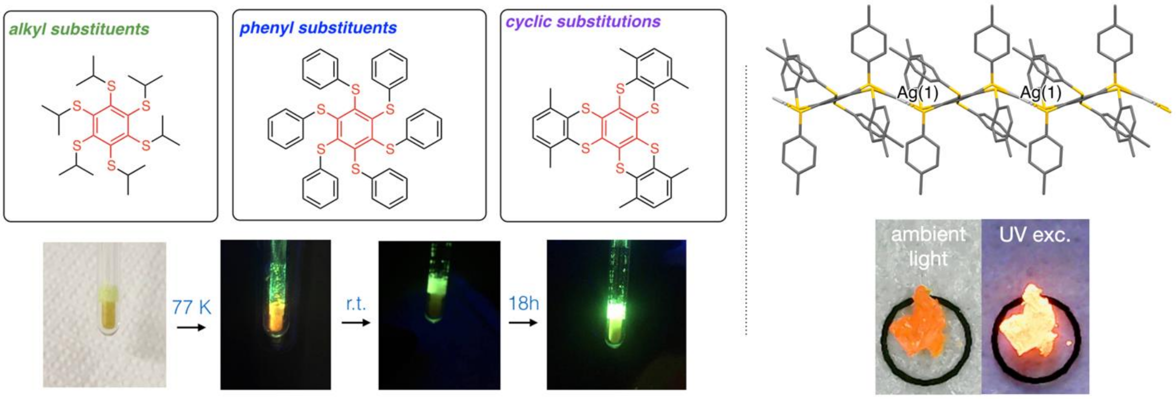
High intensity and long-lasting room temperature phosphorescence from molecular solids is regarded as one of the most intriguing properties for molecular materials, due to their countless application in information security, biological imaging, optoelectronic devices, and intelligent sensors.[1] Despite the relatively large amount of known and available organic phosphors, the design of emissive solids at room temperature and the full comprehension of the photophysical phenomena affecting the lumincescence performances of such emitters still represent a challenging task. Phenyl-substituted persulfurated benzenes have been reported as strong organic phosphorescent emitters in the solid state at room temperature.[2-3] Recently, we have taken into account a family of phenyl-, alkyl-, and polycyclic substituted persulfurated benzene in order to rationalize their behaviour as organic emitters.[4] We investigated in detail the photophysical properties of these materials, highlighting their remarkable dependence on the physical state of the sample (crystalline *vs.* amorphous phases; low *vs.* room temperature). The analysis of the luminescence of amorphous samples at low temperature has evidenced an intricate combination of several factors – *i*) presence of intermolecular interactions, *ii*) conformational disorder, and *iii*) nature of the electronic transition involved – that has been elucidated with the help of theoretical calculations. Furthermore, the interaction with Ag^+ ions allows the formation of solid-phase emitting coordination polymers, able to show peculiar photophysical properties dependent on the structural geometry adopted.



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P36

CONSTRAINED HBED DERIVATIVES: A NEW POTENTIAL CLASS OF GALLIUM-68 CHELATORS FOR PET APPLICATIONS

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Positron Emission Tomography (PET) is a widely used diagnostic technique that relies on specific biological molecules labeled with a positron (β^+)-emitting isotopes for clinical imaging. The use of β^+ emitting radiometals is becoming an increasingly clinically used approach, and among them the generator-produced gallium-68 ($t_{1/2}$ = 67.7 min, I_{β^+}=89%, E = 1.92 MeV) offers advantageous features for diagnostic purposes and the direct labeling of biomolecules.

To guarantee that the emitted radiation is solely directed in proximity of the tumour site, ^{68}Ga must be tightly coordinated to the tumour-targeting molecule though a chelating agent forming a highly thermodynamically stable and kinetically inert complex. Cyclic chelators such as DOTA generally exhibit slow kinetics of metal complexation that requires harsh radiolabeling conditions (high temperature) incompatible with the majority of biomolecules used as targeting vectors. Acyclic chelators offer an intriguing alternative, in fact although their complexes generally exhibit slightly lower thermodynamic stability compared to macrocyclic counterpart, their complexation kinetics are usually significantly faster and do not require high temperatures. Among them, HBED stands out as one of the most effective coordinating agents for ^{68}Ga, displaying a markedly high thermodynamic stability ($\log\beta_1$ = 38.51). The potential N_2O_4octahedral coordinating environment can fulfil the necessary characteristics for a successful Ga^{3+} complexation [1].

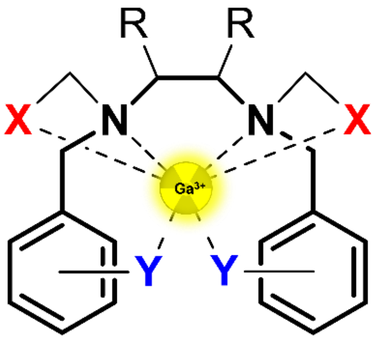

***Figure 1.** general structure of the synthesized Ga^{3+} chelators and complexes.*

In the present study, a new series of constrained HBED-based chelators have been synthesized (Figure 1) and thoroughly characterized. The stable Ga^{3+} complexes were fully characterized through ^{1}H/^{13}C NMR, LC-MS, and UV-Vis spectroscopy. The overall stability constants of the Ga^{3+} complexes were determined by UV-Vis, ^{1}H NMR and pH-potentiometric titrations, employing HypSpec[2] and/or HypNMR[3] for data processing. Stability assessments were carried out in simulated biological media such as saline and plasma at 37°C, indicating a good stability for potential applications in nuclear medicine.

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P37

RUTHENIUM COMPLEXES WITH GLUCOSYLATED LIGANDS REVEALED ABLE TO INHIBIT AMYLOID AGGREGATION OF HISTIDINE-PEPTIDES

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Neurodegenerative diseases are often characterized by the accumulation of amyloidogenic peptides and proteins, which form aggregates and contribute to the development of neurofibrillar plaques [1]. A wide range of compounds has been investigated for their potential as therapeutic agents, and within this cohort, transition metal complexes exhibit potentialities as lead compounds as neuroprotective agents [2]. Ruthenium complexes are in clinical trials for the treatment of various cancer types but, more recently, they are exploiting in neurodegenerative diseases [3].

In the present study the ability of three Ru-arene complexes, sharing three-legged piano-stool structures, to modulate the aggregation of two distinct short protein fragments was demonstrated [4]. These small fragments containing a His residue are the fragment: i) 27–32 of human Bloom syndrome protein ($BSP_{27–32}$) [5] and ii) 83-88 of human beta-2-microglobulin ($\beta 2m_{83-88}$) [6]. The effects on the aggregation processes were evaluated using ThT and Tyr fluorescence, and the direct interaction between Ru-complexes and amyloid models was analyzed by ESI-MS. In addition, their influence on the morphology of the amyloid fibers was investigated through TEM analysis. The presented results clearly demonstrated the modulating effect of investigated metal complexes opening avenues for their employment as novel neurodrugs[7].

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P38

INVESTIGATION OF Ba^{2+} AND Ra^{2+} COORDINATION CHEMISTRY: DESIGN OF CHELATORS FOR RADIOPHARMACEUTICALS

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Radium-223 (^{223}Ra, $t_{1/2} = 11.43$ d) is an α emitter suitable for the treatment of small metastatic tumours and is currently used in the form of [^{223}Ra]$RaCl_2$ (Xofigo®) for the palliative treatment of bone metastases in patients with castration-resistant prostate cancer.[1] Barium-131 (^{131}Ba, $t_{1/2} = 11.50$ d) and barium-135m (^{135m}Ba, $t_{1/2} = 28.7$ h) decay by electron capture and isomeric transition, respectively, and might be suitable ^{223}Ra-analogues for Single Photon Emission Computed Tomography imaging.[2] To enlarge the plethora of potential treatable tumours and prevent the accumulation of these calcimimetic metals in the bones, they should be stably complexed by a chelator, in turn conjugated to a biologically active moiety to direct the emitted radiation only to the tumour site. The basic coordination chemistry of Ba^{2+} and especially Ra^{2+} has not been explored to a large extent so far, hampering the rational design of proper chelators capable to firmly coordinate ^{223}Ra and $^{131/135m}$Ba *in vivo*.[3] Here we explored the coordination preferences of Ba^{2+} and Ra^{2+} in terms of affinity to different donor atoms or groups, thus setting the bases for the subsequent design and development of suitable chelators for cutting-edge ^{223}Ra- and $^{131/135m}$Ba-based radiopharmaceuticals. A series of monodentate and bidentate ligands were investigated both theoretically and experimentally. To compare the behaviour of Ba^{2+} and Ra^{2+}, the electronic binding energies (ΔE) for the reaction $M^{2+} + L^{n-} \rightarrow [ML]^{(2-n)+}$ in water (M^{2+} is Ba^{2+} or Ra^{2+}, L is the ligand, n is its charge in the fully deprotonated form) were calculated by Density Functional Theory. Ba^{2+} and Ra^{2+} behave very similarly since their ΔE are almost identical with all the investigated ligands. The thermodynamic stability constants ($\log\beta$) of the $[BaL]^{(2-n)+}$ complexes were determined either by ^{1}H-NMR titrations of L with $Ba(ClO_4)_2$ in H_2O + 10% D_2O at constant pH, or by acid-base UV-Vis or potentiometric titrations of $Ba(ClO_4)_2$ and L in H_2O. The trend of the experimental $\log\beta$ is quite in agreement with that of the computed ΔE. As expected due to the different number of donor atoms, bidentate ligands usually give more stable $[ML]^{(2-n)+}$ complexes than monodentate ones. Ba^{2+} and Ra^{2+} generally prefer more negatively charged ligands - *e.g.* 2− phosphonates > 1− carboxylates > DMSO - and oxygen rather than nitrogen or sulphur donors. Conditional stability constants ($\log\beta'$) at pH 7.4 were derived from the $\log\beta$ to consider both the metal-ligand affinity and the protonation state of the ligand. The comparison of $\log\beta'$ allowed to select a series of ligands (picolinic and malonic acid, 1,2-HOPO, catechol, and phosphonates) which are more prone to coordinate Ba^{2+} and Ra^{2+} thanks to their chemical structure or donor atoms. Polydentate chelators based on these pivotal structures are now being developed by our group to open the way towards ^{223}Ra and $^{131/135m}$Ba-labelled targeted radiopharmaceuticals.

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P39

NITROIMIDAZOLE-BASED RUTHENIUM(II) POLYPYRIDYL COMPLEXES: TURN ON THE LIGHT FOR FIGHTING ANAEROBIC BACTERIA DISEASES

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The widespread use of antibiotics has dramatically accelerated the rise of Antimicrobial Resistance (AMR) [1] making it urgent to develop effective antimicrobials that should be based on a new class of compounds rather than analogues of popular scaffolds.

In this respect, Ruthenium(II) Polypyridyl Complexes (RPCs) are prospective sources for novel antimicrobials as they offer augmented electronic properties and a rich structural diversity, providing a unique opportunity for designing effective antibacterial agents.[2]

In this communication, the well-established ability of RPCs to photorelease ligands is employed in the design of novel antibacterial agents effective under hypoxic conditions. For that purpose, Nitroimidazole-based antibiotics ($L\text{-}NO_2$) were selected according to their well-known activity as antibiotics clinically used in fighting anaerobic bacterial diseases. In particular, 5-Nitroimidazole (5NIMH) and two newly synthetized Metronidazole derivatives (MTZH-1 and MTZH-2) were incorporated on a ruthenium scaffold $[Ru(tpy)(dmp)(L\text{-}NO_2)]PF_6$ (tpy = terpyridine, dmp = 2,9-dimethyl-1,10-phenanthroline) in which the insertion of sterically hindered dmp ligand confers distorted octahedral geometry favouring the photorelease of $L\text{-}NO_2$ ligands when the complexes are directly irradiated with visible light.[3,4] This strategy enables to produce novel photoresponsive tools efficacious in the treatment, *in vitro*, of Gram-positive bacteria growth under strict anaerobic conditions, with the advantage of having precise spatial and temporal control over the drug activation ensured by light.[4] This work enables the translation of the well-known use of the RPCs in Photoactivated Chemotherapy (PACT) into the barely explored development of antimicrobials effective under therapeutically relevant hypoxic conditions. For the first time, the effectiveness of *Photorelease Antimicrobial Therap*y (PAT) was demonstrated.

***Acknowledgements*:**

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P40

FLEXIBLE TERPYRIDINE METAL−ORGANIC FRAMEWORK

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Flexible metal−organic frameworks (MOFs) are porous coordination polymers that undergo considerable structural transformation upon desolvation, and respond to a range of stimuli, that are relevant to potential applications (as gas storage, gas separations, drug release, molecular sensors and catalysis).[1]

Recently, we reported a novel flexible terpyridine MOF (Zn-terp, in Figure 1a) which, upon desolvation, transforms into the closed phase, and then to the open shape-memory phase after the first CO_2 (195 K) adsorption−desorption cycle.[2] Shape memory MOFs exhibit permanent porosity even in absence of gas molecule, and to the best of our knowledge, only five flexible frameworks are known to exhibit permanent porosity even in the absence of gas molecules. [3]

For Zn-terp we observed six phase transformations triggered by several subsequent stimuli (Figure 1b), and *in situ* experimental studies (SC-XRD and PXRD) indicated the ability to maintain permanent porosity during repeated adsorption and desorption stress. The observed phenomenon originates from the evolution of intermolecular π−π interactions between the terpyridine linkers.

Now we are investigating the effect of modification of N position in terpyridine ligand on the structure and flexibility of the obtained MOFs.

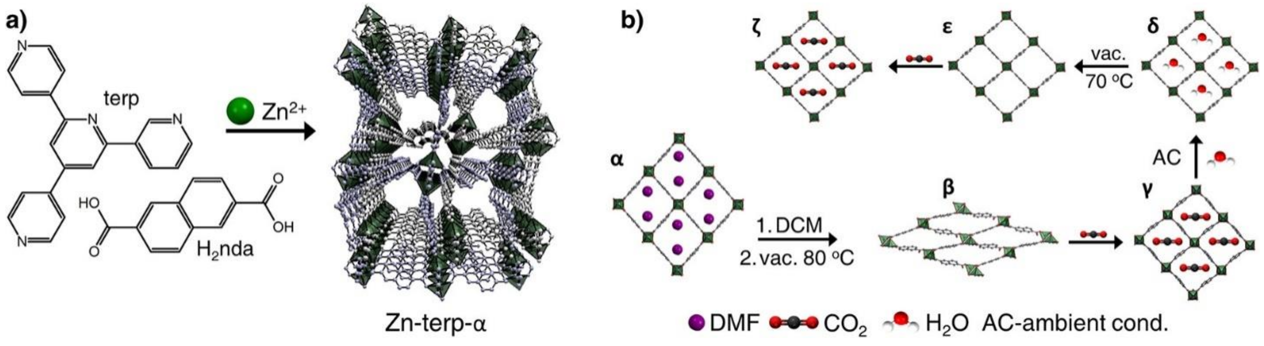

***Figure 1**: a) Synthetic route and structural features of the as-synthesized Zn-terp-α; b) schematic illustration of the phase transformation. α=$[Zn_2(nda)_2(terp)]\cdot 2DMF$, β=$[Zn_2(nda)_2(terp)]$, γ=$[Zn_2(nda)_2(terp)]\cdot 3CO_2$, δ=$[Zn_2(nda)_2(terp)]\cdot 2H_2O$ and ε=$[Zn_2(nda)_2(terp)]$; ζ=$[Zn_2(nda)_2(terp)]\cdot CO_2$.*

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TAILORING HIGH ENTROPY OXIDES FOR DAYTIME RADIATIVECOOLING

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High-entropy oxides (HEOs)[1] are a class of materials which have been recently demonstrated to possess potentiality in several technological fields, ranging from (among the others) ion-battery, photo-and electro-catalysis, to energy storage, and low thermal conductivity. The stability of such materials is ensured by increasing the number of ionic components which in turn enhances the entropic factor (ΔS_{mix}) that becomes dominant in the Gibbs free energy equation. In such interesting scenario, in the present work we discuss the potential applicability of selected oxides and of the alloys they form at different concentrations for *daytime radiative cooling* process (DRC).

Passive radiative cooling is a phenomenon that naturally occurs at night time to all sky-facing object surfaces, reducing their T without additional energy consumption. Passive coolers directly emit heat through a transparent spectral window of the atmosphere (in the 8-13μmrange) into the cold universe that acts as an infinite heat sink (T~3K). Sub-ambient surface temperature can thus be reached exploiting such process, improving indoor comfort and saving energy. Very interestingly radiative cooling has been shown to occur also at daytime[2] and can be exploited tocoolsurfacesbelowambient T even under directsunlight.

In recent years, architectures based on metamaterials and photonic structures have been suggestedfor DRC. Scarce attention anyway has been paid to any single material able to embody all the features characterizing an efficient daytime radiator. In this context we extend the possible applications of HEOs to the realm of DRC. Our detailed computational screening[3] has revealed a HEO compound, nominally $(Y_{0.25}Sc_{0.25}Ge_{0.25}In_{0.25})_2Si_2O_7$, (hereafter, YSGI) as a potentially excellent material for DRC. In particular, by combining density functional theory and the finite difference method, we report an unbiased, scattering-free description of structural, electronic, and dynamic features of YSGI and of its precursors showing the required strong radiative properties for passive cooling while offering the benefits of affordability and compatibility with commercial coating fabrication processes.

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P42

HOST-DOPANT DATIVE BONDING FACILITATES MOLECULAR DOPING IN TIN-LEAD PEROVSKITES

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Electrical doping stands as an effective pathway to attain strict control over the electronic properties of hybrid perovskite materials[1], which is crucial to ensure their optimal implementation into next-generation optoelectronics. Molecular doping has emerged as a promising route to harness charge carrier density via charge transfer without compromising the structural integrity of perovskite. Nevertheless, the details on the underlying host-dopant interactions governing such process remain elusive. In this talk, we will report on the doping mechanism of p-type methylammonium tin-lead iodide films by employing 4-(1,3-Dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl)-N,N-dimethylbenzenamine (n-DMBI-H) as an n-type molecular dopant[2]. Via a powerful combination of ab initio simulation and experimental techniques, we will describe the preferential dative bonding between amino groups in n-DMBI-H and surface Sn in perovskites as a key host-dopant interaction that facilitates electron transfer. To conclude, we will discuss the introduction of n-DMBI-Hinp-i-nperovskite solar cells, which leads to fewer recombination losses and enhanced selectivity at perovskite/transport layer contacts. Our work provides a comprehensive picture of perovskite molecular doping that will have important implications for the design of perovskite optoelectronic applications.

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P43

POLYMER/CNT COMPOSITES FOR BIOMEDICAL SENSORS INVESTIGATED BY XPS, NEXAFS AND SIMS SPECTROSCOPY

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Composites consisting of carbon nanotubes (CNTs) grafted to polymeric substrates combine the conductivity of CNTs with the visco-elastic properties of polymers and appear therefore as promising candidates to replace the classic metal electrodes with extendable and stretchable two-dimensional conductive devices. These composites have possible applications in biomedicine, from drug delivery to tissue engineering. In this framework, we have prepared new polymer/CNT composites, consisting of single-wall carbon nanotubes (SWCNT) blended to two types of polymers, showing different mechanical properties: poly dimethyl siloxane (PDMS), a thermoset polymer, and Sipolprene (SiPol), a complex polymer, whose complex chemical structure, shown in fig. 1, consists of an alternation of crystalline and amorphous domains.

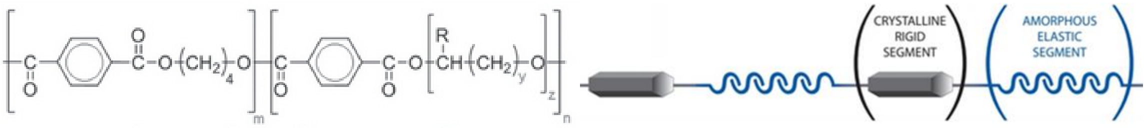

***Figure 1**: Chemical structure of Sipolprene*

The chemical and electronic structure of the PDMS/CNT and SiPol/CNT composites was investigated by different spectroscopic techniques including XPS (X-ray Photoemission Spectroscopy), NEXAFS (Near Edge X-ray Absorption Fine Structure), and TOF-SIMS (Time of Flight Secondary Ion Mass Spectroscopy), with the aim of ascertaining the chemical composition of the composite surface and the stability of the structure of polymers and CNTs. Pristine polymers and CNTs were also investigated for comparison.

***Acknowledgements*:** *Financial support from Progetto DIME Regione Lazio (POR FESR Lazio 2014-2020 PROGETTI DI GRUPPI DI RICERCA 2020, Project DIME, Grant Code PORA0375E0084 - is gratefully acknowledged.*
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Authors from the University of Rome Tor Vergata also acknowledge the University for the establishment and support of the JRU ISIS@MACH ITALIA, Research Infrastructure hub of ISIS (UK), [MUR official registry U. 0008642.28-05-2020 and U.0013837.04-08-2022].

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P44

FLUORIDE BINDING BY LN(III)-COMPLEXES: A MULTINUCLEAR AND MULTIFREQUENCY NMR STUDY

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Halide recognition by coordination complexes represents a major challenge for coordination chemistry. In particular, fluoride binding to lanthanide chelates has attracted increasing interest in recent years: it has proven to be very useful for studying the spectroscopic and magnetic properties of paramagnetic complexes, and essential for designing new responsive Ln(III) receptors.[1-4]

Here we investigate the interaction between fluoride and a series of mono-anionic Ln(III)-complexes characterized by different structure, coordination geometry and hydration numbers, with the aim of determining how the nature of the ligand affects the halide-binding. A combination of high- and low-resolution NMR techniques in the frequency and time domains enabled to characterize the kinetics and thermodynamics of the fluoride binding event, and to describe the structural, magnetic, and dynamic properties of the ternary complexes (Ln(III)-ligand-F^-).

The results of this study represent a step forward to understand the structural and dynamic properties of lanthanide chelates, and their molecular interactions with halides, which is an essential prerequisite to design new receptors with increased anion affinity and selectivity.

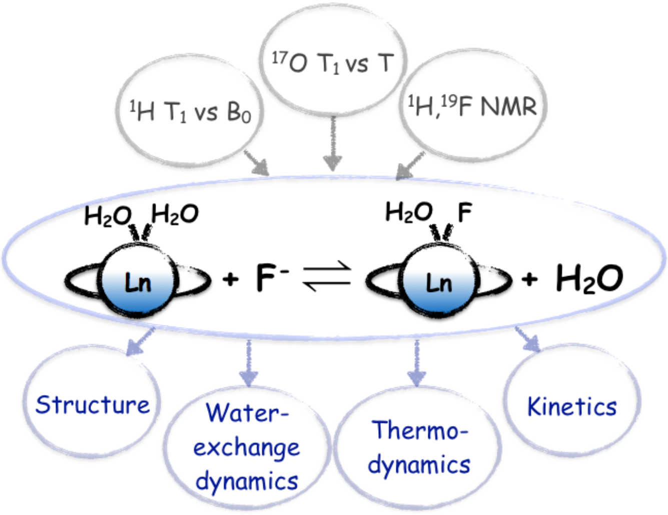

***Figure 1**: schematic representation of the main techniques used to characterize fluoride binding by lanthanide chelates, and information derived from this study.*

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P45

DEHYDROGENATION OF FORMIC ACID CATALYZED BY IRIDIUM-BASED ORGANOMETALLIC COMPLEXES HAVING PYRIDINE-AMIDE LIGANDS WITH A SUGAR SUBSTITUENT

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A current valid strategy for hydrogen storage consists in the use of organic carriers that are non-toxic and liquid at room temperature (LOHCs).[1] These substances can be obtained from renewable energy sources through a hydrogenation reaction and can be easily transported to the desired place and be dehydrogenated to release molecular hydrogen. Among the most promising organic compounds, formic acid (FA) is of particular importance, because it can be dehydrogenated to produce molecular hydrogen and carbon dioxide according to the following reaction:

$$HCOOH \rightarrow CO_2 + H_2$$

Catalysis is essential for this reaction to occur. Complexes of Ru(II)[2] and Ir(III)[3] with the classical piano stool structure have proved to be particularly effective. In the context of our studies on iridium complexes containing ligands derived from sugars, we have recently[4] demonstrated the ability of complexes **1** and **2** (Figure 1) to hydrogenate enantioselectively lactic acid and its derivatives. In this study they were tested in the dehydrogenation of formic acid in aqueous solution. The catalytic activity has been probed by systematic kinetic investigations, evaluating effect of pH, temperature, and the concentration of the catalyst and of the buffer solution. Finally, targeted experiments allowed to bring out the high durability of these catalysts.

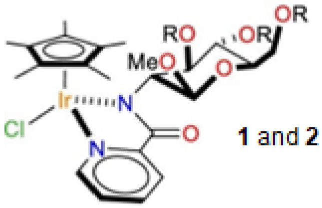

***Figure 1**: Structure of complexes **1** (R= H) and **2** (R= OAc)*

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P46

NOVEL THIENYL-SUBSTITUTED PORPHYRAZINE COMPLEXES FOR PHOTOVOLTAIC APPLICATIONS

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Tetrapyrrole macrocycles are organic molecules endowed with high interest in organic photovoltaics (OPV). Thanks to their thermal and chemical stability and to their peculiar spectroscopic properties, these macrocycles allow the creation of devices capable of converting solar energy to electricity. Recently, it has been shown that porphyrazine-type tetrapyrrolesnon-symmetrically substituted at the periphery of the macrocycle are very promising dyes for photovoltaic cells. In fact, by functionalizing thioethyl porphyrazines with a pyrene substituent, able to interact with carbon nanostructures (such as graphene and single wall nanotubes), it was possible to create nanohybrids capable of current photogeneration. In these nanohybrids thethioethyl porphyrazine is able to act both as an antenna, absorbing solar radiation, and as anelectron donor to the nanocarbon acceptor species.[1] Non-symmetrically substituted porphyrazine systems are also very promising for use as dyes in DSSC-type photovoltaic cells. In fact, good conversion efficiency has been obtained using thioethyl porphyrazine functionalized with a hydroxyphenyl group.[2] Looking for further improving of the photovoltaic performance of these materials, it was considered important to introduce a functional group, like the carboxy one, more effective in anchoring TiO_2 to the cell surface. Syntheses of carboxyphenyl- and carboxythienyl-substituted thioethyl porphyrazine systems have therefore been carried out. Among these, the thienyl systems appeared very promising as they combine the presence of ananchoring group, such as the carboxyl group, with the electron-rich thienyl heterocyclic system capable of modulating, in principle, the electron transfer between the substituent and the macrocycle. Here we report a rapid and efficient procedure for obtaining porphyrazine derivatives functionalized with a carboxythienyl group as shown in the Figure 1.

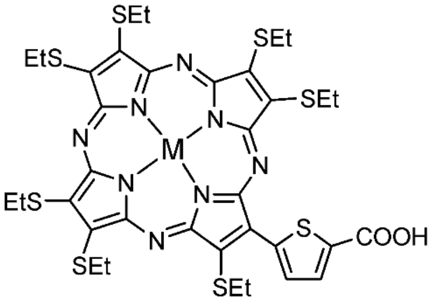

Figure1. *Structure of carboxythienyl-substituted thioethyl porphyrazine complex.*

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P47

SURFACE DEFECTS ENGINEERING ONNANO-Cu/TiO$_2$ FOR EFFICIENT HYDROGEN PRODUCTION

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H_2 production from alcohol photocatalytic reforming reaction is one of the most promising processes in the field of heterogenous photocatalysis[1]. Titania can be considered an ideal photocatalyst[2] but its wide bandgap (3.0-3.2 eV), the fast charge recombination and the presence of backward reactions are only few factors that can negatively affect the development of H_2 production at a large scale. Tuning TiO_2 optical and electronic properties, by means of metal co-catalyst loading and by working on chemical surface composition can be a promising strategy to overcome these limits. The use of Cu co-catalyst can hinder the fast charge-carriers recombination, and surface defects engineering can improve the overall photocatalytic efficiency, enhancing the separation of the photocarriers, promoting the sacrificial agent adsorption, and extending the light absorption range[3]. In this work, surface defects engineered nano-Cu/TiO_2 ($Cu_{2.0}$/gOx/P25X) photocatalysts have been synthesized through an easy and cost-effective microwave-assisted hydrothermal synthesis, followed by Cu co-catalyst loading through in-situ photodeposition procedure during reaction. Correlations between the photocatalytic activity and both physicochemical and optical properties of the materials have been established, by means of several techniques and $Cu_{2.0}$/gOx/P25X photocatalysts have been successfully used for hydrogen production through methanol reforming, showing an increased reactivity compared to bare $Cu_{2.0}$/P25 system (Fig. 1).

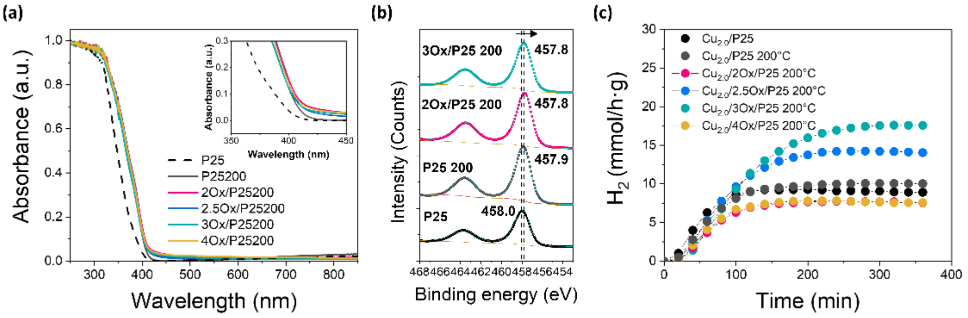

***Figure 1**: **(a)**DRUV-vis absorbance spectra of gOx/P25200 series samples. **(b)** Ti2p X-ray photoemission spectra for P25, P25200, 2Ox/P25200 and 3Ox/P25200 samples. **(c)** Photocatalytic H_2 production rates under UV light irradiation.*

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P48

CLASSIFICATION OF BIOMOLECULAR STRUCTURES BY INVARIANT SHAPE AND DEFORMATION PARAMETERS

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The classification of biomolecules according to structural similarities is an relevant issue in biochemistry[1], recently attracting an increasing interest boosted by the upcoming big data era. Proper choices of parameters, containing invariant structural information, could possibly induce, upon systematic exploration, convenient mapping and grouping of structures depending on predominant structural motifs or also individual amino acid geometry and connectivity properties[2]. Here, we give a summary of the theoretical background of parameter derivation from many-body hyperspherical coordinates and extend a previous work based on the use of shape parameters and deformation indexes. Such parameters are derived from "symmetric" hyperspherical coordinates and applied to a large set of protein structures and carbon nanostructures, each represented as a network of nodes. Different choices for the network nodes are also investigated.

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P49

A THEORETICAL CHARACTERIZATION OF THE REACTION MECHANISM AT THE MICROSCOPIC LEVEL FOR BIMOLECULAR REACTIONS LEADING TO THE FORMATION OF INTERSTELLAR PHOSPHORUS- AND SILICON-BEARING MOLECULES.

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Silicon and phosphorus, together with carbon, oxygen, hydrogen and nitrogen, are among the most important elements in the interstellar medium (ISM). Silicon in the form of silicates is one of the main constituents of the core of dust grains, while the chemistry of phosphorus has strong implications for prebiotic chemistry. In recent years, phosphorus simple compounds have been clearly identified in the coma of comet 67P/Churyumov-Gerasimenko[1] and in different regions of the interstellar medium, including the shocked region L1157-B1, where PO and PN are the main P-bearing compounds[2,3]. The presence of silicon in the gas phase is mainly related to violent events, such as shocks caused by young stars. As soon as silicon is released in the gas phase, it can immediately react and it is mostly converted into SiO, which is considered a useful target to probe shock regions[4]. Interestingly, in the same L1157-B1 shock region, another rarer Si-bearing molecule (silicon sulfide, SiS) has been detected with a surprisingly high abundance in a well-localized region around the protostar, suggesting a different chemical origin for SiO and SiS[4]. Given the difficulties associated with the experimental investigation of most of the postulated interstellar reactions, theoretical quantum chemistry calculations appear to be essential to elucidate the chemistry of silicon-bearing and phosphorus-bearing species. In the present contribution, we present new analysis of the reaction mechanism at the microscopic level for the possible formation pathways of interstellar PO, PN, and SiS, focusing on ion-neutral reactions. In details, after an initial investigation through *ab initio* calculations, we perform a kinetic analysis using a RRKM code implemented by us to derive the rate coefficients and branching ratios. The use of a semi-empirical(Improved Lennard-Jones) formulation for the initial long-range interactions allows us to obtainmore reliable values of the rate constantto include in current astrochemical models. The reactions rate coefficients will be used in astrochemical models in collaboration with C. Ceccarelli (Institut de Planétologie et d'Astrophysique de Grenoble).

Acknowledgements: *This project has been carried out thanks to a research grant founded by the project "Formazione di molecolecomplessenellospaziointerstellare". The project has received funding from the Italian MUR (PRIN 2020, "Astrochemistry beyond the second period elements", Prot. 2020AFB3FX)and by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 811312 for the project 'Astro-Chemical Origins' (ACO).*

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P50

FINE-TUNING THE SYNTHESIS OF TIO$_2$ NANOPARTICLES THROUGHDOE (DESIGN OF EXPERIMENT) MODEL

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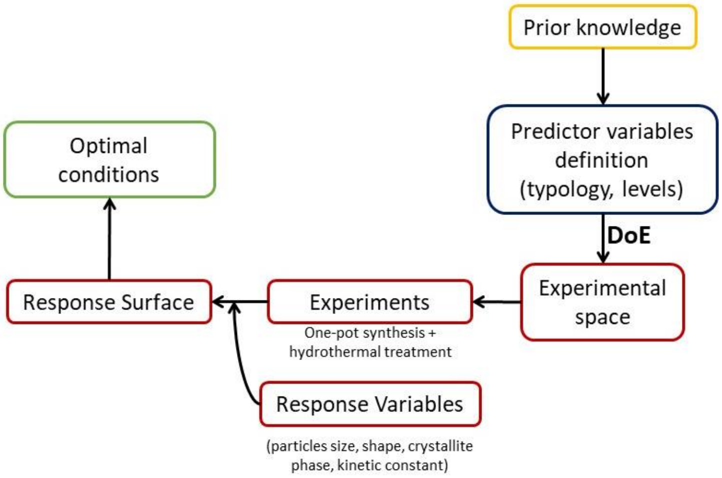
A Design of Experiments (DoE), a statistical approach to experimental planning[1], was employed to optimize the preparation of TiO$_2$ nanoparticles through one-pot synthesis and subsequent hydrothermal treatment. Key properties, namely particle size, shape, crystallite phase, and kinetic constant, were considered in constructing the response curve and determining the optimal synthesis conditions. Differentparameters including precursor type, surfactant/precursor ratio (W), pH environment, surfactant concentration (C), and calcination temperature were selected and adopted as predictor variables[2,3]. Preliminary results obtained using the computed model demonstrated that W and precursor type influenced the particle shape and size. Moreover, the concentration of hydrochloric acid and calcination temperature also played a crucial role in determining the presence of crystallite phases. The synthesized particles were initially obtained as amorphous white powder. The particles were then transformed into rutile and anatase phases at 400 °C, with further conversion to the stable rutile phase at 600 °C.



***Scheme 1**. Diagram of the experiment design process*

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P51

PREPARATION AND CHARACTERIZATION OF COBALT SUBSTITUTED GLOBINS

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Over the last few years, cobalt coordination compounds have been widely studied as catalysts for the production of green hydrogen by water electrolysis[1]. However, these compounds present some drawbacks like their low water solubility. As a consequence, cobalt coordination compounds have been embedded into protein scaffolds as non-native cofactor to solve these problems and improve the efficiency[2].

In this context, we have substituted the natural heme*b* group of two proteins belonging to the class of globins (myoglobin and neuroglobin) with Co(III)-protoporphyrin IX to obtain the corresponding Co-adducts, whose reactivity was studied with a combination of spectroscopic (UV-Vis, MCD and fluorescence) and electrochemical techniques.

We found that replacement of the heme group with Co(III)-protoporphyrin IX does not significantly influence the three-dimensional structure of both proteins. UV-Vis and MCD spectra demonstrate that the Co-derivatives of myoglobin and neuroglobin invariably contain a low spin, octahedral Co^{3+} ion, regardless the nature of the axial distal ligand[3].

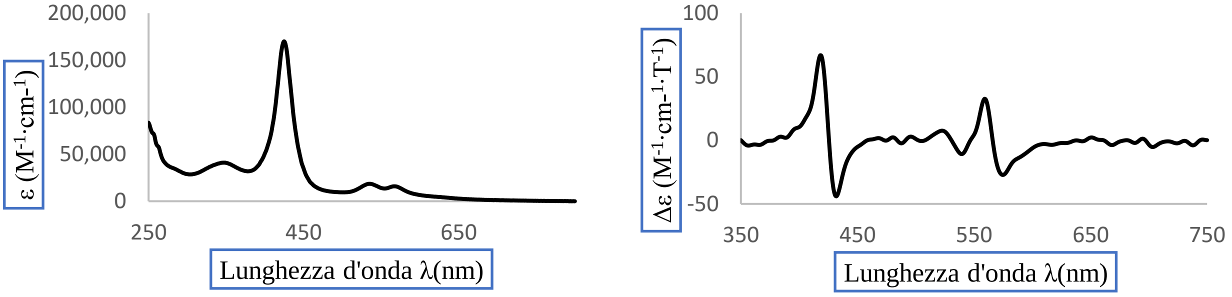

Figure 1: *Electronic (left) and MCD (right) spectra of Co^{3+}-HMbWt at pH = 7.0.*

Using cyclic and square wave voltammetry, we have been able to study the redox properties of Co(III)/Co(II) couple inside the proteins, determining its thermodynamic and kinetic behaviour.

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P52

LOW-TEMPERATURE CHEMORESISTIVE SENSING OF ACETONE BY PORPHYRIN-SnO_2 HYBRIDS

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The sensing of gas molecules is of fundamental importance for the control of chemical processes, environmental monitoring, and non-invasive medical diagnostics based on human’s breath analysis.[1] Acetone is a biomarker of type I diabetes, since its concentration in breath varies from 300 to 900 ppb in healthy people to more than 1800 ppb for diabetics. Therefore, the development of small, hand-held devices for reliable and continuous real-time measurement at room temperature of acetone would be a desirable outcome, also from a commercial point of view. Chemoresistive gas sensors are promising candidates, due to their high sensitivity, portability, compactness, low costs, sufficient limit of detection and ease of fabrication. Currently, however, the most used materials for chemoresistive gas sensors are n-type and/or p-type Metal Oxides Semiconductors (MOS) which require high temperature to work properly.[2] Recently, the combination of MOS with porphyrin sensitizers has attracted increasing attention as an easy way to improve the sensitivity of the sensors by reducing the fast electron-hole recombination processes and consequently the working temperature of these devices.[3,4] The present contribution deals with the preparation of two Zn(II)porphyrin-SnO_2 hybrids, and the investigation of their properties by electrochemical, spectroscopical and computational methods. After deposition of the composites on an interdigitated platinum electrode by air-brush, the sensing performances of the final devices are studied at mild temperatures after LED light photoactivation, to recognize the best combination for high-performing sensing materials able to reduce the acetone sensing temperature by guaranteeing acceptable LOD values. Our findings produce useful insights for the rational design of porphyrin complexes and the engineering of hybrid materials having specific surface features for enhanced sensing properties.

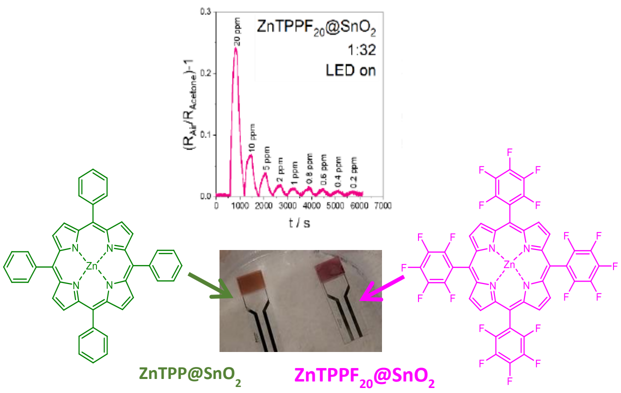

***Figure 3:** Porphirin@SnO_2 gas sensors*

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P53

SYNTHESIS OF Al_2O_3@ZnO BINARY FILLER TO COUPLE THERMAL CONDUCTIVITY AND SELF-HEALING FEATURES OF CARBOXYLATED NITRILE RUBBER

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From 2018 EU is trying to reach ambitious goals to reduce the use of raw materials and waste production towards a more sustainable model known as the circular economy.[1] In this context, smart materials which are capable of automatic healing after suffering external damages, appear promising alternatives to fulfil the reduction of waste production. Carboxylated nitrile rubber (XNBR) is an interesting candidate for the design of self-healing composites, thanks to the potential weak and dynamic bonds promoted by nitrile and carboxylic groups in the presence of inorganic filler nanoparticles (NPs), giving rise to reversible polymer networks [2]. ZnO NPs have already been exploited to dynamically crosslink XNBR by ionic-rich domains where ideally Zn^{2+} ions are coordinated by COOH groups of XNBR[3]. However, the high filler loadings necessary to achieve good healing performances, leads to particle aggregation into the polymeric composites, that limit the interactions with the carboxylic groups of XNBR, thus reducing their healing properties.

In this work, the goal was to develop a novel ZnO-based filler system to improve the self-healing capabilities of XNBR composites, to increase their service-life, sustainability and safety. A binary filler based on ZnO NPs supported on Al_2O_3 nanorods was realized by coprecipitation approach, aiming at enhancing ZnO particle distribution into XNBR to prepare high-loaded XNBR composites. Alumina was chosen as a support thanks to its good reinforcing properties as well as good thermal conductivity (λ), that could simultaneously assist to overcome permanent damages due to overheating effects in rubber composites. The filler was characterized by TEM, ICP-OES, and DRS analysis, evidencing the formation of ZnO NPs with an average diameter of 5 nm homogeneously distributed on Al_2O_3 nanorods with micrometric length and width of ~ 200 nm (aspect ratio > 10). Then they were utilized as proof of concept to produce XNBR composites, which were characterized in terms of mechanical and λ properties. Healing efficiency was calculated by the ration between tensile strength after and before healing process. The inclusion of ZnO/Al_2O_3 filler in XNBR leads both to an enhanced λ (up to + 62% at 30 parts per hundred rubber, phr, of filler) and healing efficiency (>100%) compared to unfilled rubber. Thus, the ZnO/Al_2O_3 filler activates healing mechanisms without hindering the intrinsic thermal conductivity of Al_2O_3. Further in-depth studies will be performed to complete the understanding of the interaction between the ZnO/Al_2O_3 filler and XNBR.

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P54

COMPUTATIONAL MODELING OF PEROVSKITE FOR PHOTOCATALYSIS

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While instability in aqueous environment has long impeded employment of metal halide perovskites for heterogeneous photocatalysis, recent reports have shown that some particular tin halide perovskites (THPs) can be water-stable *and* active in photocatalytic hydrogen production. To unravel the mechanistic details underlying the photocatalytic activity of THPs, we compare the reactivity of the water-stable and active $DMASnBr_3$ (DMA = dimethylammonium) perovskite against prototypical $MASnI_3$ and $MASnBr_3$ compounds (MA = methylammonium), employing advanced electronic–structure calculations. We find that the binding energy of electron polarons at the surface of THPs, driven by the conduction band energetics, is cardinal for photocatalytic hydrogen reduction.[1] In this framework, the interplay between the A-site cation and halogen is found to play a key role in defining the photoreactivity of the material by tuning the perovskite electronic energy levels. Our study, by elucidating the key steps of the reaction reported in Figure 1, may assist in development of more stable and efficient materials for photocatalytic hydrogen reduction.

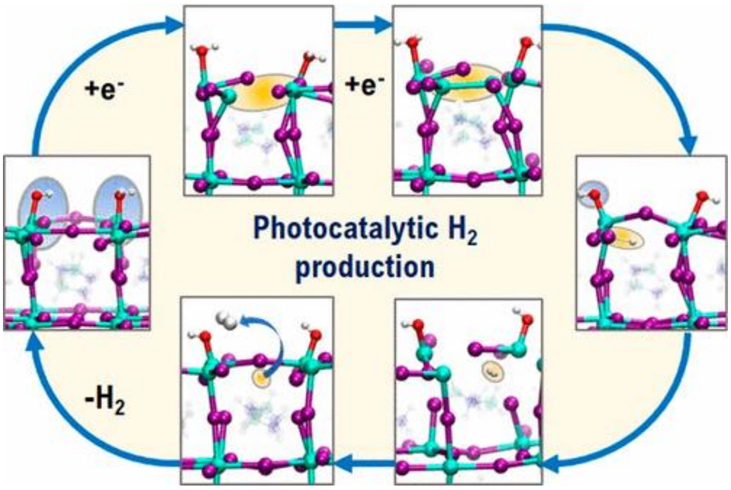

Figure 1*: caption (Times New Roman, 10 pts, centred, Italic)*

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P55

NEW [OSSO]-TYPE CHROMIUM (III) COMPLEXES FOR COPOLYMERIZATION AND TERPOLYMERIZATION OF EPOXIDES WITH CARBON DIOXIDE AND PHTHALIC ANHYDRIDE

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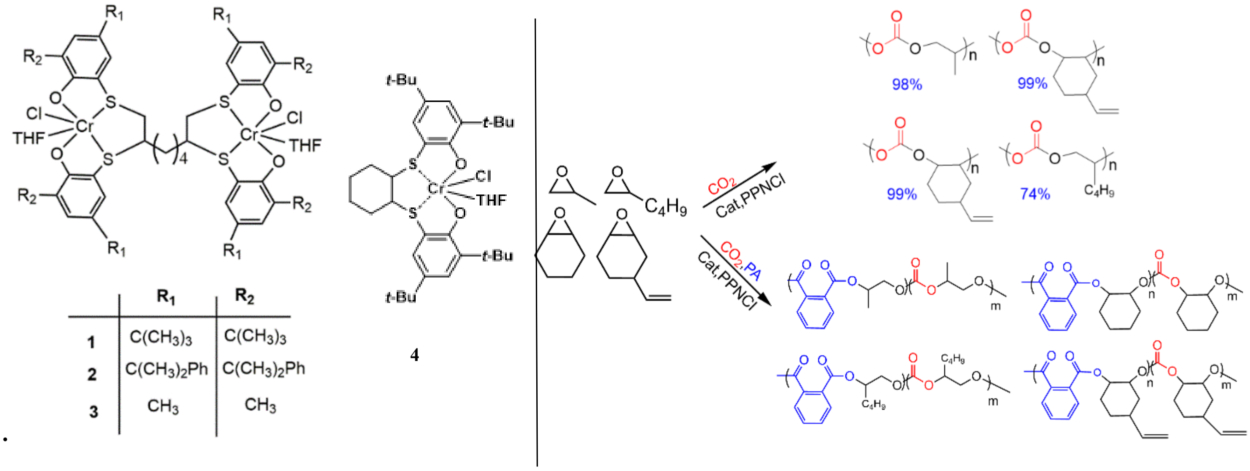
Carbon dioxide (CO_2) has been used as a nontoxic, abundant, and inexpensive C1 feedstock for polymer synthesis since the discovery of epoxide/CO_2 copolymerization by Inoue et al. in 1969.[1]The result of these types of reactions is the production of valuable cyclic organic carbonates (COCs) or aliphatic polycarbonates (APC).The design of efficient metal catalysts with the help of proper co-catalyst for the selective coupling of epoxides and carbon dioxide has received increased attention over the past decade and it can be considered as a strategy to overcome the great thermodynamic stability and kinetic inertness of CO_2.[2]

In this study, a new family of dinuclear chromium complexes (**1-3**) and mononuclear **4** containing bis-thioether-diphenolate ligands has been introduced for the binary copolymerization of carbon dioxide and epoxides and ternary copolymerization of the latter with phthalic anhydride. The catalysts in combination with nucleophile bis(triphenylphosphine)iminium chloride (PPNCl) as co-catalyst were utilized in catalytic CO_2/epoxide copolymerization. In catalytic system of **1**, selectivity toward the polycarbonate was higher than 95% in the cases of propylene oxide (PO), cyclohexene oxide (CHO), and 4-Vinyl-1-cyclohexene 1,2-epoxide (VCHO). Polyester-*b*-polycarbonates were synthesized during catalyticterpolymerization of CO_2/epoxide/phthalic anhydride (PA) for **1**, **2**,and **4**for all epoxides. Moreover, the kinetic study of formation of poly(propylene carbonate) by **1**/PPNCl as catalytic system was investigated with in situ Attenuated Total Reflection Infrared (ATR-IR) spectroscopy. The kinetic equation was found to be k=v.[**1**][CO_2]



	R1	R2
1	$C(CH_3)_3$	$C(CH_3)_3$
2	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$
3	CH_3	CH_3

Figure 1: *The [OSSO]-type Cr(III) complexes* ***1-4*** *(left); CO_2/epoxide Copolymerization and CO_2/PA/epoxide terpolymerization (right)*

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P56

EFFECT OF THE SURFACE FUNCTIONALIZATION ON ALUMINA-BASED FILLERS FOR ENHANCING THE THERMAL CONDUCTIVITY OF POLYMERIC NANOCOMPOSITES

Roberto Nisticò,[1] Massimiliano D'Arienzo,[1] Andreia Amighini Alerhush,[1] Lorenzo Mirizzi,[1] Sandra Diré,[2] Giulia Fredi,[2] Andrea Dorigato,[2] Emanuela Callone,[2] Silvia Mostoni,[1] Barbara Di Credico,[1] Roberto Scotti[1]

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One of the main relevant limitations of the use of polymer-based materials in modern technological applications (e.g., electronics and optoelectronics, photonics, automotive) is their intrinsic low thermal conductivity that does not allow polymers to counteract the occurrence of the thermal degradation due to the in-service overheating phenomenon.[1]
To overcome this thermal constraint, polymer-based materials containing highly thermally conductive fillers are receiving great attention as they show an improved heat dissipation ability. However, recent studies report that a significant improvement of thermal conductivity in polymeric nanocomposites can be achieved only at high filler loadings, but this negatively affects both the mechanical behavior and density of the materials.[2] Moreover, to achieve an efficient heat management, a continuous network of thermally conductive fillers crossing the entire composite is mandatory. In this context, interfacial phenomena play a major role as they favor the homogeneous distribution of the conductive fillers within the polymer matrix. In a previous study, it has been already verified that the surface functionalization of inorganic fillers (i.e., silica) with Polyhedral Oligosilsesquioxane (POSS) units, a family of hybrid inorganic-organic systems composed of an inorganic core of cage-like silicon oxide and several organic functional groups, significantly improved the dispersion and compatibilization of the inorganic fillers in the polymer matrix.[3]
Hence, the present contribution reports on the recent results obtained by introducing different types of alumina-based hybrid fillers decorated at the surface with either metacrylate silane or octa-methacryl-POSS units at low filler loadings in a polybutadiene polymer matrix. Even if displaying a modest intrinsic thermal conductivity, alumina can represent a valid and appealing thermally conductive filler, due to its low cost, stable chemical performance and negligible toxicity. The promising results obtained for these hybrid ceramic fillers foreshadow their potential application in large-scale formulations.

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P57

HARNESSING THE POTENTIAL OF HETEROJUNCTION BETWEEN C_3N_4 AND ZNO IN PHOTOCATALYSIS FOR THE REMOVAL OF CECS

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Transition metal oxides are crucial semiconductors utilized in photocatalytic reactions due to their remarkable stability in various environments, coupled with their relatively low or affordable cost. In the pursuit of ground breaking materials for this field, the focus lies on identifying systems with an appropriate electronic structure capable of effectively utilizing solar radiation, particularly visible light, while also exhibiting excellent potential for carrying out the desired redox processes. It is practically unattainable to find all these characteristics in a single system. Solid materials with wide band gaps generally possess favourable reduction and oxidation potentials; however, they necessitate high-energy photons for efficient charge separation. Conversely, semiconductors with narrower band gaps, suitable for visible light absorption, often exhibit unsatisfactory potentials for both reduction and oxidation. One potential solution to overcome this limitation involves modifying a semiconductor with a relatively wide band gap to enable visible light absorption or to create active interfaces between different materials.Among the various avenues explored to enhance photocatalytic performance, heterojunctions have emerged as a powerful strategy. In this regard, the heterojunction between carbon nitride (C_3N_4) and zinc oxide (ZnO) has attracted considerable interest owing to the synergistic effects arising from their unique electronic properties and complimentary band structures[1]. In this work we provide an in-depth analysis of the role of the C_3N_4-ZnO heterojunction in photocatalysis, elucidating its mechanisms, key properties, and recent advances. The objective of this study is to comprehensively explore the potential of this heterojunction and highlight its significance in advancing photocatalytic technology.C_3N_4, a two-dimensional layered material, has exhibited remarkable photocatalytic properties owing to its unique electronic structure, chemical stability, and abundance of surface active sites. ZnO, on the other hand, is a wide bandgap semiconductor known for its excellent photocatalytic activity and stability[2]. The combination of these two materials in a heterojunction holds great potential for synergistic effects, such as enhanced charge transfer and extended absorption range, enabling effective utilization of solar radiation and improved photocatalytic performance. These properties have been used to describe the fundamental principles governing heterojunction formation, charge transfer mechanisms, and the impact of interface engineering on photocatalytic efficiency. Furthermore, recent results in the abatement of clozapine, an antipsychotic drug have been reported.

Acknowledgements**:** *This work has received funding from the European Union's Horizon 2020 Research and Innovation Programme under the MarieSkłodowska-Curie Grant Agreement No101007578 (SusWater).*

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P58

AN EXPERIMENTAL INVESTIGATION OF THE REACTION MECHANISM AT THE MICROSCOPIC LEVEL FORBIMOLECULAR REACTIONS INVOLVINGATOMIC OXYGEN AND UNSATURATEDNITRILES

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The characterization of the reaction mechanism at the microscopic level is of utmost importance to understand the forces at play during elementary reactions and, in turn, to understand the chemical evolution of various media. The inclusion of elementary reactions in chain mechanisms allows one to develop reliable kinetic models to be applied in a variety of fields, ranging from combustion to astrochemistry. Particularly interesting for combustion environments are the reactions involving atomic oxygen in its ground electronic state, $O(^3P)$, and unsaturated hydrocarbons. Typically, these aremultichannel reactions in which the nonadiabatic transition (*intersystem crossing*, ISC) from the entrance triplet to the underlying singlet potential energy surface (PES) plays a central role by opening new competing reaction channels. To determine the primary products, their relative yields (*branching fractions*, BFs), and the extent of ISC, one of the most powerful experimental tools is the crossed molecular beam (CMB) scattering technique, equipped with universal electron-impact ionization mass-spectrometric detection and *time-of-flight* (TOF) analysis.[1]
In this contribution, wepresent experimental results on the $O(^3P,^1D)^+$ cyanoacetylene (HCCCN) and $O(^3P,^1D)^+$acrylonitrile (CH_2CHCN) reactions. The presence in our atomic oxygen beam of a small percentage of atomic oxygen in the first electronically excited state $O(^1D)$ has allowed us to disentangle the reaction dynamics of both electronic states. Interpretation of the experimental results and elucidation of reaction mechanisms have been assisted by electronic structure calculations of the triplet/singlet PESs and statistical RRKM estimates of product BFs. According to our results we can state that:*(i)* The $O(^3P)^+$ HCCCN reaction exhibits a minor adiabatic channel leading toOCCCN+H (BF=0.10±0.05), while the dominant channel (BF=0.90±0.05) occurs *via*ISC to the underlying singlet PES forming ^{1}HCCN+CO. The $O(^1D)$ reaction exhibits the same two channels, with the relative CO/H yield slightly larger.[2]*(ii)*The $O(^3P)+CH_2CHCN$reaction leads to two main product channels: *(a)* CH_2CNH (ketenimine)+CO (dominant, BF=0.87±0.05), formed *via* efficient ISC, *(b)* HCOCHCN+H (BF=0.13±0.05), occurring adiabatically on the triplet PES.The $O(^1D)$+acrylonitrile reaction mainly leads to the formation of CH_2CNH+CO adiabatically on the singlet PES.[3] Being cyanoacetylene and acrylonitrile two of the nitrogen-bearing compounds formed by thermal decomposition of pyrrolic and pyridinic structures present in heavy fuels, our results are expected to be useful for improving models of combustion environments.

Acknowledgements*:We acknowledge support from Italian MUR, University of Perugia within the program "Department of Excellence-2018-2022-Project AMIS".*

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P59

SELECTIVE ETCHING OF SILVER SHELL ON GOLD NANOSTARS FOR LSPR AND SERS DETECTION OF Fe(III) IONS: A MULTICHANNEL APPROACH

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Iron is one of the most common and important elements on earth and it plays critical roles in many natural and biochemical processes [1,2]. Iron concentration is therefore an important parameter for water environmental quality and, with the rapid development of modern industry, this topic is gaining more and more relevance, as recommended by World Health Organization. Convenient, rapid, high sensitive and on-site iron determination is thus important for environmental safety and human health, and nanotechnology may offer some options. In this regard, we developed a sensing system for the detection of Fe(III) in water, based on 7-mercapto-4-methylcoumarine (MMC) stabilized silver coated gold nanostars (GNS@Ag@MMC) [3], exploiting a redox reaction between the Fe(III) cation and the silver shell of the nanoparticles. When Fe(III) is added to the colloidal suspension of GNS@Ag@MMC, oxidative etching of silver can take place, with a decrease of the silver shell thickness as a function of Fe(III) concentration. As a consequence, this device can detect Fe(III) by simultaneously monitoring changes in both Localized Surface Plasmon Resonance (LSPR) and Surface Enhanced Raman Scattering (SERS) spectra of GNS@Ag@MMC, tracking the progressive consumption of the silver shell, as:

- The LSPR features caused by the presence of the silver shell in GNS@Ag@MMC, as the concentration of Fe(III) increases, gradually decreases until the spectra returns to the LSPR bands typical of original GNS;
- The SERS signals of MMC also gradually decrease as Fe(III) increases, as removal of silver shell caused a decrease in Raman signal enhancement when reverting to GNS [3].

The specific selectivity of the system towards Fe(III) has been verified investigating the LSPR and SERS response to the presence of other cations.

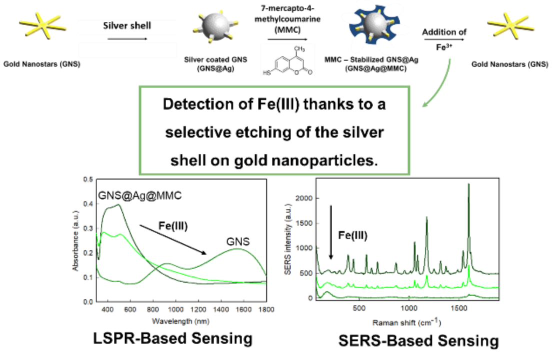

Figure 1: *Schematic representation of GNS@Ag@MMC synthesis and LSPR and SERS-based detection of Fe(III).*

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P60

Zn(II) AND Cu(II) BINDING TO THE C-TERMINAL REGION OF ACE2 RECEPTOR: THE RECOGNITION INTERFACE OF ACE2 FOR SARS-COV-2 SPIKE PROTEIN

Massimiliano F. Peana,[1] **Alessio Pelucelli**,[1]**Bartosz Orzel**,[2] **Karolina Piasta**,[2]**Elzbieta Gumienna-Kontecka**,[2] **Serenella Medici**,[1] **Maria Antonietta Zoroddu**[1]

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The coordination ability of Zn(II) and Cu(II) ions with selected peptide fragments from the C-terminal region of ACE2 receptor, that play a crucial role in the binding with spike (S) protein of SARS-CoV-2, has been investigated by a combination of potentiometry, UV-Vis, CD, and NMR spectroscopic techniques. Three selected sequence models were studied: P29-38 (Ac-L_{29}DKFNHEAED_{38}-NH_2), P23-42 (Ac-E_{23}QAKTFLDKFNHEAEDLFYQ_{42}-NH_2), and P19-42 (Ac-S_{19}TIEEQAKTFLDKFNHEAEDLFYQ_{42}-NH_2). The C-terminal region of ACE2 contains specific amino acids that are involved in the interaction with S protein. This specificity is critical for the virus to establish a systemic infection and cause COVID-19 disease. This fragment is abundant in coordination residues such as aspartates, glutamates and histidine that could be targeted by metal ions. The ability of the human ACE2 receptor to coordinate metal ions, such Zn^{2+}, in the same region where it binds to the S protein could have a crucial impact in the mechanism of recognition and interaction of ACE2-S with consequences on their binding affinity that deserve to be investigated. This study confirmed the bioinformatic previsions obtained by MIB2, which evidenced a specific region (D30-Glu37) in the recognition interface of ACE2 for S protein for Zn(II) and Cu(II) binding (Figure 1)[1]. Both metal ions can change the peptide conformation, which rearranges itself upon coordination with zinc and copper. Such structural modifications might interfere with the recognition mechanism of ACE2 and the S protein, also considering that some of the residues taking part in or being perturbed by metal coordination play a crucial role in hydrogen bond formation between the two proteins.

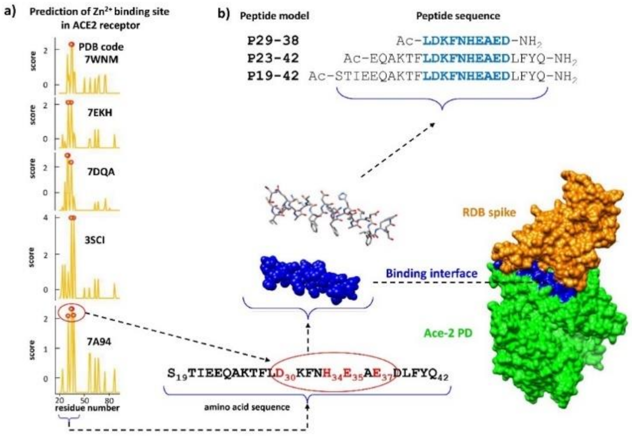

Figure 1*: a) MIB2 prediction of Zn ion-binding sites from a selection of ACE2 X-ray structures. The residues recurrent in all predictions are located in the binding interface between ACE2 and the S protein, localized in the fragment 30-37 aa; b) selected peptide fragments of the binding interface of ACE2 analysed in this study.*

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P61

GOLD AND SILVER NANOPARTICLES FUNCTIONALIZATION INTO FLUORESCENT NANOMATERIALS

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Gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) were hugely studied due to their exceptional electrical, optical, and photo-thermal properties. AuNPs and AgNPs find several applications in different fields, *e.g.*, biomedical imaging, sensors, optoelectronics [1, 2, 3].

In this work, hydrophilic AuNPs and AgNPs were functionalized with different thiols in mixture, *i.e.*, sodium 3-mercapto-1-propanesulfonate (3MPS), 6-amino-1-hexanthiol hydrochloride (6EA), cysteamine (Cys-FITC) derivatized with fluoresceine isothiocyanate (FITC) organic dye, or 4-Aminothiophenol derivatized with the same dye (Ani-FITC).

Au or Ag Nanoparticles were synthesized following a bottom-up method using $HAuCl_4$ or $AgNO_3$ as metal precursor and $NaBH_4$ as reducing agent with the co-presence of hydrophilic and dye derivatized thiols. The obtained nanoparticles have 10-20 nm size range with good colloidal stability in aqueous conditions thanks to the presence of the charged end groups on the thiols.

After careful characterization by UV-visible, FT-IR, and XPS spectroscopies, ^{1}H-NMR, dynamic light scattering (DLS) and ζ-potential measurements, it was possible to assess their optical properties, surface functionalization, size, and stability and compare with their morphological evaluation by field-emission scanning electron microscopy (FE-SEM). It is noteworthy, that the Fluorescence spectroscopy evidenced a shift of the emission peak after interaction of the FITC dye in the functionalizing layer of the nanoparticles. Due to their small size and high stability in water, the synthesized NPs are excellent candidates for applications bioimaging and sensors.

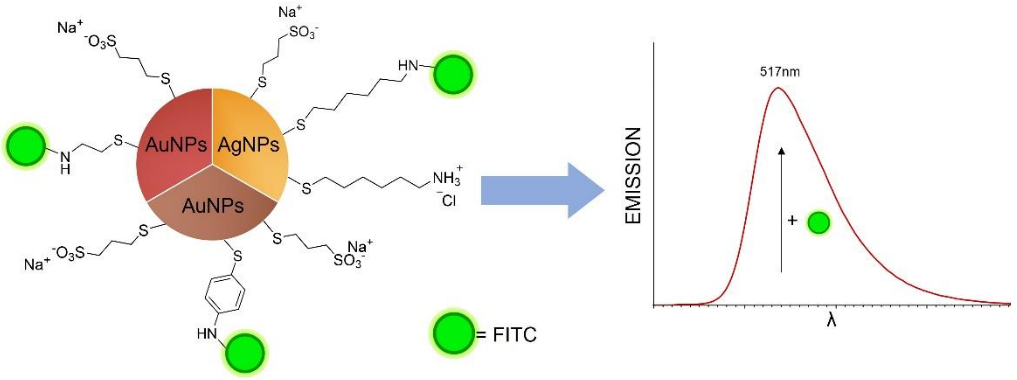

Figure 1: *Schematic representation of AuNPs and AgNPs and their emission features.*

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P62

AQUEOUS SYNTHESIS OF TWO-DIMENSIONAL LAYERED DOUBLE HYDROXIDES

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Layered double hydroxides (LDHs) are a class of anionic clays consisting of positive charged brucite-like layers spaced by water molecules and counterbalancing anions[1]. In particular, LDHs based on the first row of transition metals have recently drawn attention due to their (electro)photocatalytic properties[2]. In our work, we propose an environmentally friendly synthesis procedure able to produce two-dimensional LDH materials. The formation of single layer nanosheets is confirmed by X-ray diffraction and atomic force microscopy analyses[3]. Lastly, the nature of the ligand field transitions in the electronic spectra of nickel-aluminium and nickel-iron LDHs will be described in detail, by providing accurate ligand filed parameters and the nephelauxetic rations of nickel and iron in LDH crystal lattices. We believe that our results may lead to more advanced ligand field engineering strategies for future (electro-)catalyst designs.

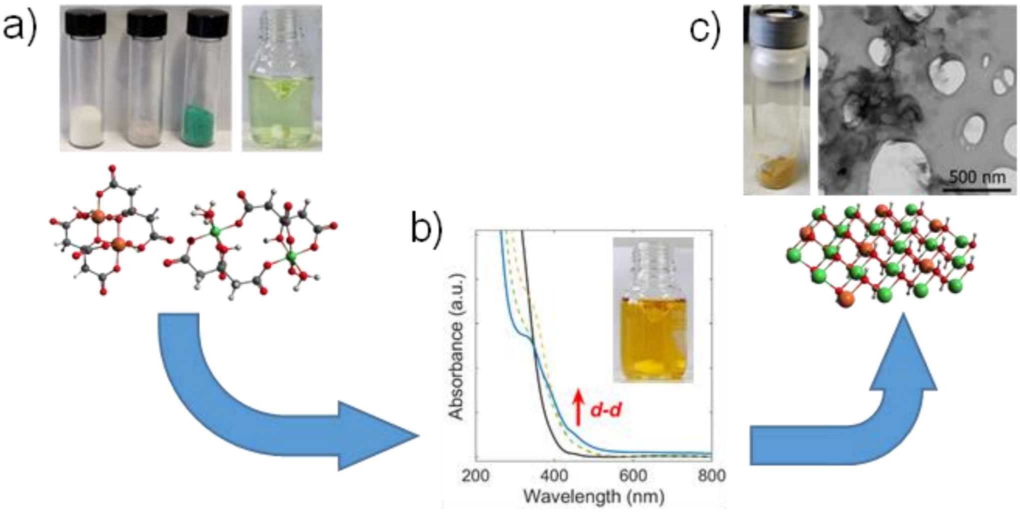

Figure 1*: Synthesis process of LDHs. a) Nickel and iron citrate coordination compounds. b) The polymerization of citrate coordination compounds leads to an absorbance increase of d-d transitions. c) The nanostructured LDH product is collected and characterized.*

Acknowledgements:*Liberato Manna, Michele Ferri, Gabriele Bianca, Andrea Griesi, Sergio Marras, Lea Pasquale, Francesco De Donato, Filippo Drago, Gabriele La Rosa, Simone Nitti, Giammarino Pugliese, Elisa Mantero, Sebastiano Bellani.*

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P63

INSIGHTS IN MOLECULAR UPCONVERSION: POLYNUCLEAR LANTHANIDE COMPLEXES CASE

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Upconversion (UC) is an intriguing optical phenomenon in which low energy photons are converted in more energetic ones. This peculiar property is finding cutting edge applications in the energy conversion as well as in biomedical field, thanks to the near infrared water transparency window conveniency to reach deep tissues.[1] Upconversion on the molecular scale has a strong potential to provide precisely controllable upconversion materials without the drawbacks related to nanoparticles. On the other hand, a major impediment to the actual application of molecular upconversion systems is the lack of knowledge of their upconverting behaviour. As an example, it is commonly believed that highest sensitized cooperative UC efficiencies can be obtained by high ratios of sensitizer-to-activator ions. Using nonanuclear hetero-lanthanide complexes, we demonstrated both experimentally and theoretically that interion distances are more relevant and that highest upconversion efficiencies are attained for approximately equal amounts of sensitizers and activators. Moreover, we identified the cooperative sensitization as the main UC mechanism determining the complexes brightness, while the energy migration as the phenomenon determining the UC kinetics.[3]

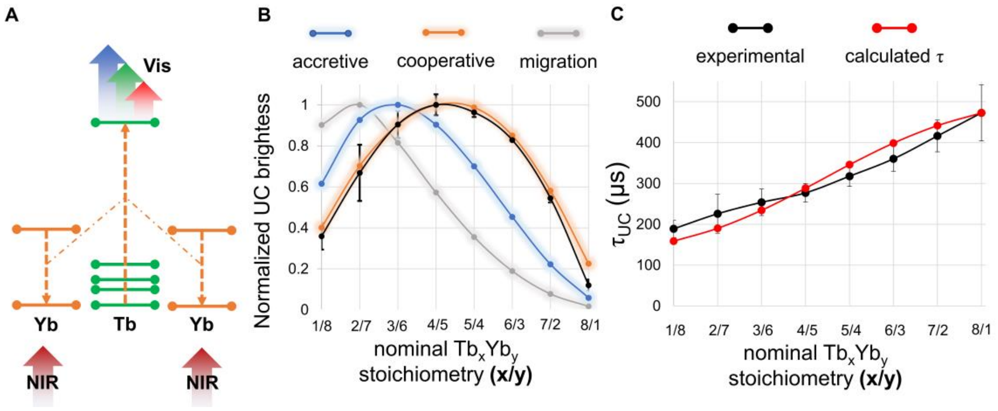

***Figure 1**: A) General cooperatively sensitized upconversion scheme for Yb-Tb system. B) Normalized experimental and calculated (for different mechanisms) UC brightness versus nominal stoichiometry for the different nominal stoichiometries of the complexes. C) Lifetimes of the UC emission for the different nominal stoichiometries of the complexes.*

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P64

ANISOTROPIC SILICA-BASED NANOMATERIALS FROM RENEWABLE FEEDSTOCK

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In the last few years, anisotropic inorganic nanomaterials raised great interest for applications in high performance nanocomposites, including elastomeric compounds for tires. In particular, silica is one of the reinforcing fillers widely used to enhance the mechanical properties, i.e. elastic modulus and elongation at break. Nanoparticles (NPs) with high aspect ratio (AR) produce the so-called filler network when embedded in elastomers, which consists of an oriented anisotropic filler interconnected structures, through both direct particles interactions and their bridging by polymer chains. It has been demonstrated that the filler self-assembly of rod-like silica[1] and silicate nanofibers[2] in nanostructures inside the rubber matrix provides a larger amount of bounded rubber at filler-rubber interface, further enhancing the amount of overlapping rubber layers and thus improving the mechanical properties. These results suggest the possibility of tuning the formation of the filler network improving the filler-rubber interaction by using high AR fillers. The most popular class of AR nanomaterials is represented by clays, thanks to the high availability of the original minerals. However, clays used in fundamental studies as well as industrial application are today mainly derived from mines, resulting in limited possibilities to tune their geometric properties, and leading also to possible concerns related to accidental mineralogical impurities.

In this scenario, the present work aims to develop a new family of high AR nanomaterials, like natural clays, from renewable feedstock, exploring a range of dimensions not accessible starting from the natural origin minerals and avoiding any possibility of contamination with critical impurities. The synthesis of NPs with a controlled AR was explored starting from silicate wastes and rice husk has been taken into consideration as silica precursor. In fact, rice husk is a food industry by-product which contains huge amounts of chemically severable silica, which would allow the circular economy realization, by avoiding raw materials exploitation and by reducing CO_2 emissions due to less energy-intensive processes compared with extraction ones. In detail, an aqueous precipitation of anisotropic magnesium silicate was performed in hydrothermal conditions, without using any synthetic template. The conditions necessary for the precipitation of anisotropic silicate were optimized by changing reaction time and temperature, as well the concentration of reagents. An exhaustive multi-technique characterization of the materials has demonstrated the possibility to obtain anisotropic NPs.

The following step will focus on the evaluation of the influence of anisotropic nanofillers on structural, morphological and mechanical properties of elastomeric nanocomposites in respect to the filler properties, such as amount, size, shape and surface chemistry.

Acknowledgements: *F.P. thanks CORIMAV (Consortium for the Research of Advanced Materials between Pirelli and Milano Bicocca University) for its support within the PCAM European Doctoral Program.*

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P65

DESIGN AND DEVELOPMENT OF SUSTAINABLE AND FUNCTIONAL INNOVATIVE COATINGS FOR TEXTILES

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One of the recent trends in the world of nanotechnology is the development of hybrid functional nanomaterials and nanocomposites, gatherings from the presence of nanometric functional components of the organic or inorganic type, which when suitably dispersed in a polymeric matrix, allow the obtainment of a product with improved performance compared to those of all the starting components. Modern innovative approaches involve the development of advanced nanostructured materials that can be used as surface coatings or in various forms for a wide range of industries [1].Among these, those concerning the smart and high-tech textile sector are of great importance [2]; the development of new functional coatings for textile substrates is in fact key in order to confer implemented properties, such as antifouling or antibacterial, hydrophobic, anti-stain, fire-retardant, controlled release of drugs, detection of molecules, mechanical resistance.In this regard, the sol-gel method must certainly be counted among the new sustainable and versatile synthetic approaches [3]. Thanks to its advantages, such as the low process temperature, the high homogeneity of the final products, the absence of cytotoxicity and the high versatility of the corresponding silanic precursors, also characterized by the ability to bind stably to molecules or to various substrates, they allow the new functional obtained coatings by use of eco-friendly and non-cytotoxic solvents and reagents for the environment and human health [4].

In this work, sustainable sol-gel procedures are reported, based on the use of (3-glycidyl-oxypropyl) trimethoxysilane (GPTMS) and various functional alkoxysilanes, employed for the treatment of textile substrates (cotton and polyester), in order to confer different functional properties. In particular, the synergistic function between the roughness and the reduced surface energy induced by the alkylsilanes suitably selected for the sol-gel functionalization, has allowed the obtainment of different hybrid coatings with excellent new implemented properties. These sustainable coatings are therefore of key importance for all those hydrophilic substrates, such as cotton, to give them properties such as to make them suitable for applications in technical fields and related to well-being and everyday life, or in the sectors of sensors, environmental remediation and biomedicine. In this study the potential applications and performances of these advanced materials, useful as they are, or as surface coatings, will be shown in terms of environmental, economic, and social impact.

***Acknowledgements**: The research work was conducted within the framework of "Made in Italy Circolare e Sostenibile (MICS)" funded by MUR and provided by the European Union under the NextGenerationEU program-PNRR Mission 4 "Education and Research".*

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P66

COMPUTATIONAL AND EXPERIMENTAL STUDY OF VANADIUM(V) SPECIES IN AQUEOUS SOLUTION

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The research in vanadium redox flow batteries has seen an intense growth during the last decade. A variety of studies has been focused on optimization of electrodes performances, selectivity, and conductivity of membranes, etc. Recently the attention has been focused on the optimization of solutions in terms of thermal stability and energetic density.

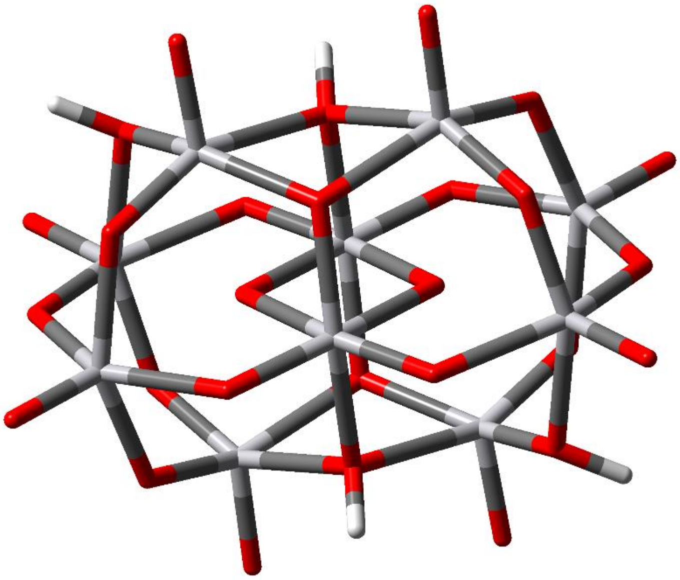

Figure 1: *DFT optimized structure of the* $[H_4V_{10}O_{28}]^{-2}$ *ion*

In this work the stability of the Vanadium(V) species in aqueous stabilized using betaine as supporting electrolyte is studied by experimental, spectroscopic, and computational techniques.
All the utilized techniques converge to confirm the existence and stability of $[V_{10}O_{28}]$ anionic species with different levels of protonation.
The stability and structure of these species are studied at the DFT level and compared with experimental results, especially FTIR spectra. The details of the interaction of betaine zwitterions with these large anions is also studied.

Acknowledgements: *The financial support of the INSTM consortium is here acknowledged.*

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GOLD(I/III) PEROVSKITES FOR PHOTOVOLTAIC APPLICATIONS: FROM MOLECULAR STRUCTURE TO INTERMOLECULAR INTERACTIONS

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In the last decade, an enormous amount of work has been focalized on the analysis, synthesis and optimization of new perovskite materials for their very promising photovoltaic properties. The main mazterials are based on lead(II) halides, but with problems of stability in the real atmosphere and possible toxicity.[1] For these reasons, many combinations of +1/+3 metal centers have been analysed with very different performances. Recently, a new focus on mixed oxidation state gold halide perovskites reappeared.[2] Although the purely inorganic examples are known from a lot of time, very few organic-inorganic perovskites have been reported, and their use in photovoltaic show very interesting results. However, no one perform an in dept study on the forces of this solid, both at a molecular level or at a supramolecular level. In this work, we present a clean synthesis of four polymorphic ammonium and alchilammonium perovskites, their crystal structure and stability. At the same time, we performed calculation to demonstate the distribution of the charges into the gold(III) unit, in the framework of the inverted ligand field theory, and with QTAIM, NCI plots and ELF analysis, we manage to characterize the halogen/coinage Au···I contacts, that are at the basis of this family of solids.[3] We are sure that the results will shed new light on this fascinating and promising materials.

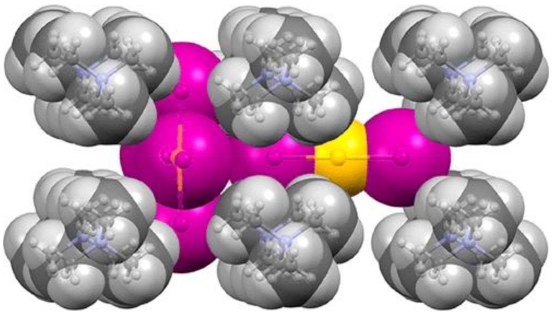

***Figure 1**: anion-anion interaction in tetrametylammonium derivative*

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P68

PROMISING METALLO-B-LACTAMASES INHIBITORS AS ANTIBIOTIC ADJUVANTS

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Metallo-b-lactamases (MBLs) are zinc enzymes capable of hydrolyzing β-lactams, which are one of the most potent and commonly prescribed classes of antibiotics [1].

Today, the absence of inhibitors for these enzymes, combined with their recent spread and evolution, raises serious concerns about the effective treatment of infectious diseases. This is especially so due to the resistance to carbapenems, which are a last resort for multi-drug-resistant bacterial infections [2,3].

A strategy to face the increase in resistance is identifying MBL-resistant-β-lactams, or MBL inhibitors that could act as antibiotic adjuvants, restoring β-lactam antibacterial activity [4].

In this work, several clinically used drugs and new R- and S-2-amino-3-(1H-imidazol-4-yl)-N-[2-(pyridine-2-yl)-ethyl] propenamide have been studied as potential inhibitors against MBLs. Specifically, the ability of these compounds to restore the antibacterial activity of Meropenem (MEM) was investigated. To do so, a time-dependent inhibition screen of the compound set was performed on New Delhi metallo-beta-lactamase 1 (NDM-1) and Verona Integron–encoded Metallo-β-Lactamase 1 (VIM-1) producing *K. Pneumoniae*. The synergistic activity between MEM and compounds exhibiting inhibitory activity against MBLs was further studied using a checkerboard assay. Among them, Chlorpropamide, an antidiabetic drug, demonstrated an ability to restore the antibacterial activity of MEM at micromolar concentrations against VIM-1-producing *K. Pneumoniae*.

Acknowledgements**:** *The authors acknowledge support from funding within the NextGeneration EU-MUR PNRR Extended Partnership initiative on Emerging Infectious Diseases (Project no. PE00000007, INF-ACT).*

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P69

NANOSTRUCTURED POLYMER-BASED MEMBRANES FOR SUSTAINABLE WASTEWATER REMEDIATION

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The health and wellbeing of humans and other living species is highly related on water sources. Unfortunately, the availability and security of sources of drinkable and potable water are increasingly threatened by urbanization, anthropological activities, and the growing global population. Additionally, the regeneration of wastewaters is becoming increasingly difficult due to the presence of new emerging pollutants coming from industrial and agricultural activities. Therefore, a quick and effective action is required to prevent and address water pollution. On this regard, membrane-based approaches are now used for the filtration and remediation of polluted water, such as ceramic, polymeric, porous and non-porous membranes that employ the application of pressure to retain various contaminants and/or desalinate water. Through a rational design and in order to increase the performances of such filtration systems, membranes can be produced starting from different functional blended polymers doped with proper cross-linkers, stimuli-responsive systems or nanofillers[1]. Subsequently, by innovative approaches like electrospinning, for example, it is possible to obtain electrospun nanofiber membranes[2] featuring different advantages compared to conventional porous membranes. Additionally, the most common petroleum-derived polymers for the development of these lasts should be replaced with more sustainable formulations, which is necessary in order to prevent a secondary source of pollution and a risk to human health and ecosystems. In particular, this communication deals about the design and development of smart and sustainable bio-polymeric blends employed to produce different membranes by the non-solvent induced phase separation process and electrospinning technique. Moreover, in order to achieve better features and selectivity against the adsorption of specific wastewater organic contaminants, a stimuli-responsive polymer and different eco-friendly functional nanofillers were employed as dopant agents of the starting polymeric blends. Finally, chemical-physical and structural-morphological characterizations concerning all the dopant agents and obtained functional membranes, as well as the removal tests of two organic dyes are reported.

Acknowledgements: *PON-MUR "Ricerca e Innovazione 2014–2020" RESTART innovative PhD funding project is gratefully acknowledge.*

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P70

NOVEL Bi-HPDO3A CONTRAST AGENT FOR X-RAY COMPUTED TOMOGRAPHY

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Novel compounds for CT imaging with high X-ray attenuation capability and low biotoxicity are desirable[1]. ^{209}Bi element is a good candidate due to the higher attenuation coefficient than Iodine, the mostly used element for the design of clinical CT agents[2]. This work aimed at preparing and testing *in vitro* and *in vivo* a novel small agent, Bi-HPDO3A, as a potential CT agent for the urinary system.
Bi-HPDO3A was synthesized and characterized by UPLC-MS and NMR spectroscopy (1H, 13C). Transmetallation was investigated at 305 nm in presence of Zn^{2+} ion. For cell viability, MTT assay was carried out on J774 cells (Bi-HPDO3A 0-500 µM, 24 h). Solutions at different Bi^{3+} concentrations (3-400 mM) were prepared and *in vitro* CT imaging was carried out (MiLabs VECTor^6, 65 kV). Isovue-370 (iopamidol) was used as a control at the same concentrations of Iodine. Healthy mice (n = 3) were scanned before and after the *i.v.* injection of Bi-HPDO3A (1.2 and 5 mmol/kg) and images were acquired within 1 hour. *In vivo* control experiments were performed by administrating iopamidol (1.2 mmol/kg). Kidneys HE staining was performed to investigate potential organs damage at 5 mmol/kg of Bi-HPDO3A. Bi-HPDO3A showed a good stability under the presence of Zn^{2+} and cell viability was around 80% even at high Bi(III) concentration. The *in vitro* CT performances of the complex were evaluated against iopamidol. A linear regression was observed between CT values and agent concentration. The good *in vitro* performances of Bi-HPDO3A, which showed a very high water solubility, were also confirmed *in vivo*, where the complex was administered to healthy mice. As shown in Figure 1, Bi-HPDO3A was rapidly excreted by urinary system, as expected. Bi^{3+} may represent an alternative to iodine-based CT agents because of the higher X-ray attenuation capability. The good *in vitro* stability and *in vivo* CT performance of Bi-HPDO3A at different doses proved its potential for kidneys and bladder CT imaging.

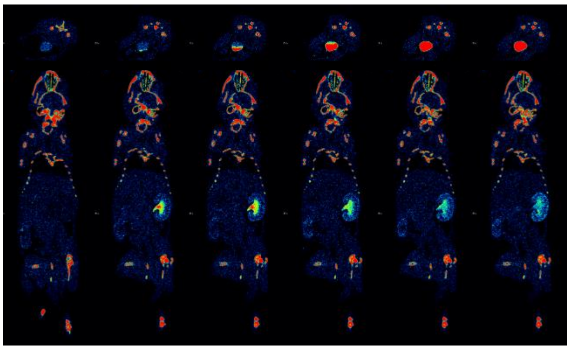

Figure 4. *In vivo CT imaging (1.2 mmol/kg Bi-HPDO3A).*

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P71

STRUCTURE AND REACTIVITY OF $[LAu(\mu\text{-}H)_2MCp_2][X]$DIHYDRIDES (M = Mo, W): EXPLORING LIGAND AND ANION EFFECTS

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Gold hydrides have been postulated as key intermediates in several heterogeneous and homogeneous catalytic reactions.[1] However, the intrinsic instability of the Au-H bond makes them difficult to isolate and only a few cases of stable molecular gold hydrides are known.[1,2] A suitable strategy to improve their stability is to trap them in bridging bimetallic complexes. In this respect, some of us showed recently that bridging $LAu(\mu\text{-}H)_2WCp_2^+$ species offer a stable and versatile platform to study the interaction between a cationic gold center and an hydride donor with pontential for photochemical hydride transfer.[3]

In this contribution, we will report the synthesis of a wide class of heterobimetallic compounds with a $Au(\mu\text{-}H)_2M$ core modulated by different M fragments (W and Mo dihydrides) and ancillary ligands (N-heterocyclic carbenes and phosphines with different electronic and steric properties). In particular, we will show how these factors affect structure, stability and spectroscopic features of the bimetallic adducts $[LAu(\mu\text{-}H)_2MCp_2][SbF_6]$ (Figure 1). Furthermore, using the BF_4^- counterion (Figure 1) instead of SbF_6^- allowed us also to understand the relative charge distribution on these cations by NOE NMR and rationalize their behaviour in photochemical hydride transfer reactivity under UV or VIS irradiation. We will also show how our experimental results are backed up by DFT calculations.

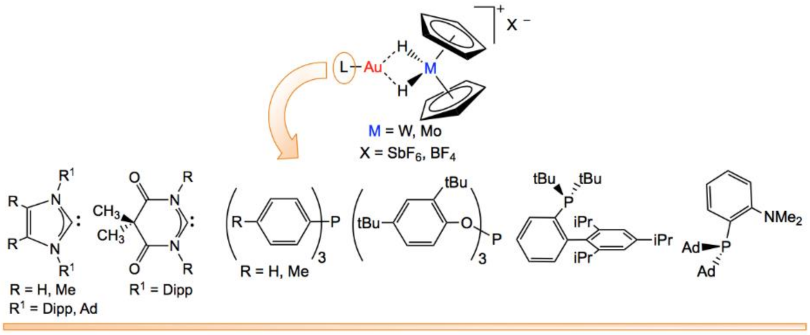

Figure 1: *Heterobimetallic Au-H_2MCp_2 adducts studied in this work*

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P72

2,3-DIHYDROISOINDOLINONE CHELATING PHARMACOPHORE FOR THE INHIBITION OF BUNYAVIRAL ENDONUCLEASE

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The order Bunyavirales encompasses various families of segmented-negative strand RNA viruses, posing a significant public health concern.[1] All bunyaviruses, in analogy with influenza virus, possess an essential endonuclease domain responsible for viral replication. This domain coordinates two divalent metal ions, magnesium or manganese, which are crucial for cap-snatching catalytic activity.[2] The chelation strategy has been proven to be a successful approach for the development of efficient endonuclease inhibitors: some chelating compounds can efficiently coordinate the metal cofactors blocking enzymatic activity and preventing viral replication. In the present work, a series of 2,3-dihydroisoindole derivatives previously disclosed as influenza virus endonuclease inhibitors[3] was synthetized and characterized (**Figure 1**). The interaction between a model 2,3-dihydroisoindole derivativeand Mg(II) or Mn(II) ions in solution was studied by means of visible spectrophotometric titrations, in order to determine the binding constants. The enzymatic activity was tested on two different Cap-Endonucleases of the *Bunyavirales*order: all the compounds exhibited inhibition activity towards the investigated enzymes, with IC_{50} values in the low micromolar range. The interaction between one of the inhibitors and Toscana Virus endonuclease has been studied by Isothermal Titration Calorimetry and the corresponding binding constants have been determined, highlighting the crucial role of the divalent cations in the inhibition mechanism.

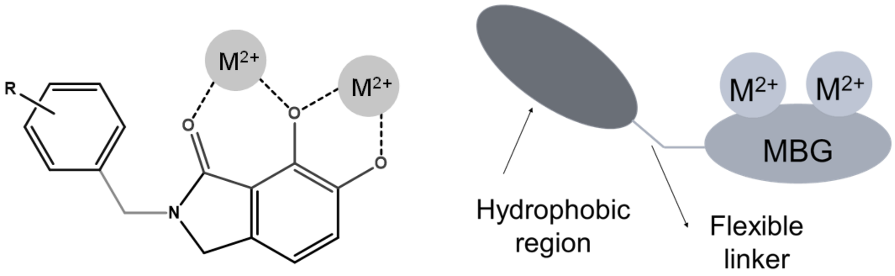

Figure 1: *Schematic representation of the 2,3-dihydroisoindolinone chelating scaffold. MBG: metal binding group.*

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[2] J. Reguera, F. Weber, S. Cusack, *PLoSPathog.***2010,** 6,DOI:10.1371/journal.ppat.1001101.
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P73

POLYDOPAMINE COATED GOLD NANOSTARS: TOWARD SERS PLATFORMS

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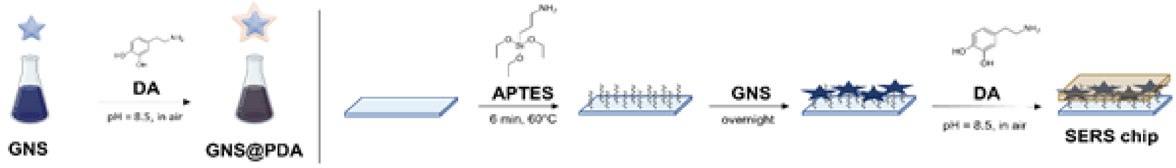

***Figure 5**: a schematic representation of the formation process of SERS active nano-objects (GNS) both in colloidal suspension and on chip*

Here in this contribution, we describe the process of coating of gold nanostars (GNS) with an ultra-thin layer of polydopamine (PDA) and we present a rich characterization of the obtained objects, both on colloidal suspension and grafted on a chip. The goal is to exploit the adhesive properties of PDA[1] - to increase the affinity towards target molecules - and the sensitivity of Surface Enhanced Raman Spectroscopy (SERS) to enable their detection at low concentration level. A proper evaluation of the thickness of the PDA layer is crucial to exploit its adhesive properties while keeping the precious SERS enhancement, which is strongly dependant on the distance of investigated analytes from noble metal surfaces.
The thickness values obtained with spectroscopic ellipsometry and transmittance on PDA coated quartz chips can be compared with the decreasing SERS intensity from Rhodamine 6G (R6G), used as Raman probe, on GNS@PDA substrate as a function of thickness. Scanning Electron Microscope (SEM) images, surface Z-potential and UV-visible spectra were collected to complete the characterization of the SERS chip. The obtained results are fundamental in the perspective of future applications for pollutants detection employing SERS.

At the same time, self-polymerization of dopamine was exploited to coat GNS in colloidal suspension. Again, these GNS coated with PDA layers of increasing thickness were obtained and characterized by means of Transmission Electron Microscopy, Dynamic Light Scattering and UV-visible spectroscopy. Finally, we investigated the SERS response of GNS@PDA towards R6G.

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P74

SYNTHESIS OF ALKALINE-EARTH METAL AMIDES APPLYING THE IN SITU GRIGNARD ADDITION METHOD

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The synthesis of sterically demanding alkaline-earth metal amides is a challenging process due to the inertness of the metals. Therefore, multistep reactions, for example salt metathetical or transmetalation procedures were applied in the past. The prior formation of (heavy) *Grignard* reagents is another possibility to synthesize alkaline-earth metal amides. *Grignard* reagents cannot only be used for the metalation of H-acidic substrates but also in addition reactions to imines.[1,2] To circumvent side reactions and limitations in the formation of heavy *Grignard* reagents and to simplify the procedure, the in situ *Grignard* Addition Method has been established.[3] In this one-pot protocol the alkaline-earth metal reacts very smoothly with an organyl halide and an imine in ethereal solution. Using the iGAM, the solid-state structures of the homoleptic magnesium and calcium amides $[(Et_2O)_nAe\{N(Ph)CHPh_2\}_2]$ were characterized. To broaden the scope of the reaction, various hydryl halides and imines were tested. Hydrolysis of the reaction mixtures allows the isolation of the addition products in high yields. Two-electron reduction and aza-pinacol coupling of two imines were observed as minor side reactions. In the iGAM, calcium is the metal of choice, while the heavier alkaline-earth metals are less selective due to their higher reduction potential. Solvent screening of the reaction shows a variable product distribution. In addition to the iGAM in solution, a ball milling procedure was also successfully tested and compared with the reaction in solution.

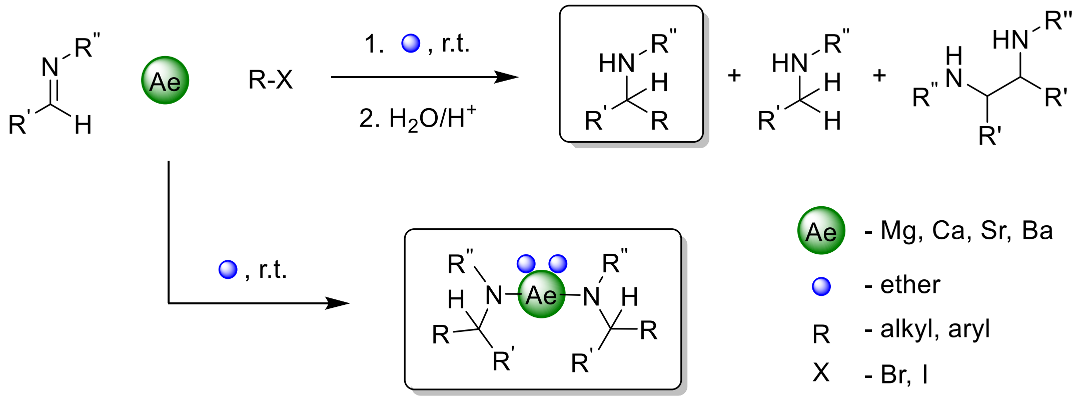

***Figure 1**: Reaction of benzylidene-aniline with phenylcalcium iodide and calcium metal leading to iGAM, reduction and aza-pinacol coupling.*

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[1] S. Krieck, P. Schüler, J. M. Peschel, M. Westerhausen, *Synthesis* **2019**, *51*, 1115-1122.
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P75

SYNTHESIS AND CHARACTERIZATION OF NEW GOLD(III) CYCLOMETALATED DERIVATIVES WITH 3-SUBSTITUTED 1-(2-PYRIDYL)IMIDAZO[1,5-*a*]PYRIDINES

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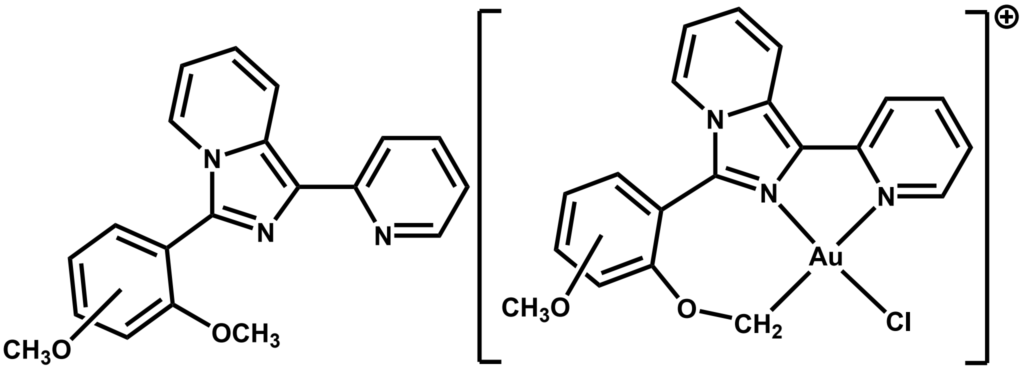
Cyclometalation, *i.e.* the intramolecular C−H bond activation facilitated by coordination of a donor heteroatom, is undoubtedly the most popular organometallic reaction leading to organometallic compounds featuring metal−carbon σ bonds. Among the many examples of cyclometalated derivatives, those containing a noble metal and a heterocyclic nitrogen ligand have attracted considerable attention due to their potential applications in many fields, including organic synthesis, homogeneous catalysis, novel materials and medicinal chemistry.[1]
Following our interest in the coordination chemistry of imidazopyridine ligands [2] here we report the synthesis and characterization of new Au(III) cyclometalated derivatives with a series of 3-arylsubstituted 1-(2-pyridyl)imidazo[1,5-*a*]pyridines in which the substituent shows -OCH_3 groups.



Activation of one of the C-H bonds of the *ortho* methoxy group leads to the formation of seven-membered cyclometalated cationic complexes featuring a C-Au bond, which to the best of our knowledge represents the first case of cyclometalation with these ligands. The new cyclometalated derivatives have been extensively characterized spectroscopically and analytically. Research is underway to obtain similar species of Pd(II)and Pt(II).

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P76

IMPROVING CYTOTOXIC ACTIVITY OF CATIONIC [Pt(η^1-C_2H_4-OR)(DMSO)(PHEN)]$^+$ COMPLEXES BY R ALKYL CHAIN LENGTH OPTIMIZATION

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The study of organometallic complexes with anticancer activity is making significant progress, giving the opportunity to discover more effective and selective drugs. We recently synthesized the cationic coordination compound [Pt(η^1-C_2H_4-OMe)(DMSO)(phen)]$^+$ (**1**), which demonstrated a broad spectrum of anti-proliferative activity [1]. Particularly, complex **1** showed a faster induction of mitochondrial apoptotic processes and enhanced antimigratory capacity with respect to cisplatin, on neuroblastoma SH-SY5Y cells [2]. This could be related to early alterations of the metabolic pathway of glutathione (GSH), generally associated with drug resistance and tumor progression, as suggested by ^{1}H-NMR metabolomic analysis [3]. Due to these interesting results, we decided to optimize the structure and hydrophobicity of complex **1**, by synthesizing a series of [Pt(η^1-C_2H_4-OR)(DMSO)(phen)]Cl {R = Me (**1**), Et (**2**), Pr (**3**), Bu (**4**), phen = 1,10-phenanthroline} complex analogues, starting from the corresponding [PtCl(η^1-C_2H_4-OR)(phen)] {R = Me, Et, Pr, Bu} chlorido precursors [4] (**Figure 1**). In our experiments, we evaluated the anti-proliferative activity of **1-4** complexes on HeLa, Hep-G2, SH-SY5Y, and SK-OV-3, in comparison with cisplatin. In this way, we observed the existence of an optimal R alkyl chain length, enhancing antiproliferative properties of the tested compounds. This was particularly evident in the cytotoxicity assays carried out with **1-4** complexes and cisplatin, on hepatocarcinoma Hep-G2 cells [4]. It resulted a higher cytotoxicity level in the case of complex **2** featuring the R = Et group substituent (**Figure 1**). Thus, cytotoxic and antiproliferative properties of considered phenanthroline derivatives **1-4** could be affected by possible lipophilicity variation related to R alkyl chain length optimization.

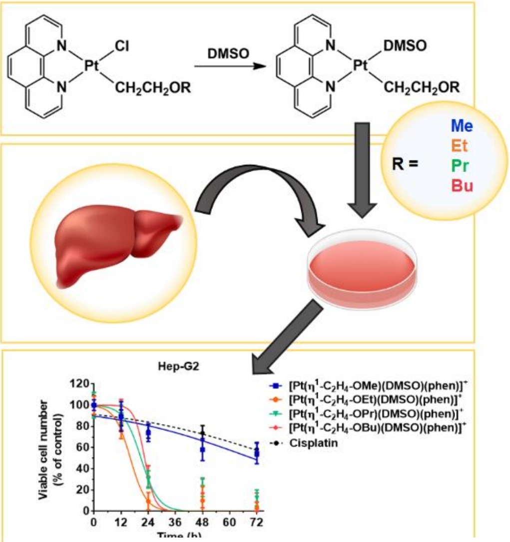

***Figure1**: Cytotoxic effects of [Pt(η^1-C_2H_4OR)(DMSO)(phen)]$^+$(R = Me, Et, Pr, Bu)*

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P77

REACTIVITY OF ENVIRONMENTAL RELEVANT Hg IONSWITH S- OR SE-CONTAINING MODEL PEPTIDES

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Mercury (Hg), present in various inorganic compounds (Hg(0), Hg(I) and Hg(II)) and organic (eg. CH_3Hg^+) forms[1] has been included by the World Health Organization (WHO) on the list of top 10most hazardous chemicals for humans, who are exposed in the workplace but mainly through diet [2]. The biomagnification of these ions is due to the affinity of Hg^{2+} and CH_3Hg^+ for the thiolgroup (soft base) ofcysteine containing proteins in biomolecules has been considered as themain reason for its high toxicity.In this study we compared the ability of all forms of mercury ions to bind sulfur and selenium containing peptide by ESI mass experiments. The reactivity of Hg(I), Hg(II) and CH_3Hg^+ chlorides were testedtoward vasopressin (AVP), anonapeptide hormone cyclized by two cysteine residues, and its mono- and diselenium analogues. The three model AVP peptides were pre-treated (30 min at 37°C) with thereducing agent dithiothreitol (DTT) and then reacted at physiological conditions (pH 7 and 37 °C)at different peptide/Hg molar ratios (from 1 to 3 eq)and incubation times (from 30 min to 18 h) leading to several metal-peptide adducts (Figure 1).Substitution of Cys by SeCys in vasopressinincreased the reactivity towards methylmercury, with the predominant formation of -Se/S-Hg-Sebridgedstructures and the consequent demethylation of methylmercury. In competitiveexperiments, CH_3HgCl reacted preferentially with the diselenium analogue rather than withvasopressin wild type. The diselenium peptide also showed the capability to displace the CH_3Hg-moietybound to S in vasopressin. These results show the greater propensity of mercury to bind selenium rather than sulfuropening a promising perspective for the use of selenopeptidesfor methylmercury coordination and detoxification strategies.

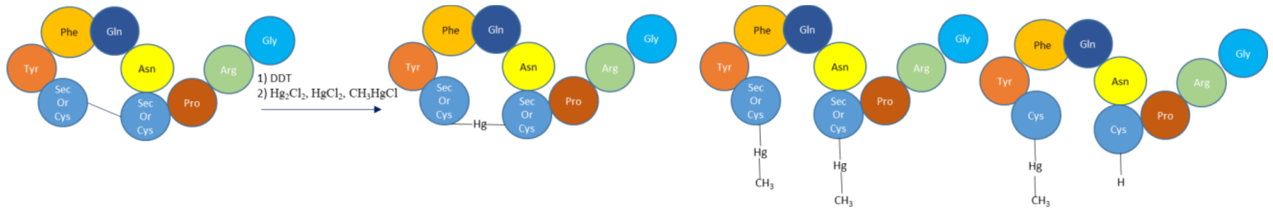

***Figure 1**: Scheme of the experiments: AVP peptides incubation with CH_3HgCl or $HgCl_2$ or Hg_2Cl_2promoting the formation of Hg-bridged peptide adducts and, with CH_3HgCl, also the mono- and bis metallatedcomplexes.*

***Acknowledgements**: Authors thank CNR for funding the Bioinorganic Drugs joint laboratory: A multidisciplinary platform promoting new molecular targets for drug discovery.*

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[2] X. Xu, et al. *Environmental Pollution***2020**, *258*, 113706.

P78

GREEN METAL NANOPARTICLES FOR SELECTIVE REDUCTION REACTIONS IN WATER

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The future development of the chemical, energetic and polymer industries is linked to the minimization/valorisation of the by-products, among which, lignin is a typical and worldwide produced waste. It is an exciting and underutilized natural polymer, of phenolic nature, that can be used as source of chemicals, additive into innovative materials or into resins.[1,2]

Recently, we prepared several metal nanoparticles (NPs) in aqueous solutions, using lignin as stabilizer and reducing agent, and we tested them as catalysts in several reactions, like oxidation, reduction and cross-coupling, reaching excellent yields and selectivities.[3-5]

Here, we will present the preparation and characterization of the Pd, Pt, Ru, and Rh NPs. In TEM images, Pd NPs appeared larger (21 nm) and spherical in shape; Pt NPs were irregular; Ru and Rh NPs were smallest (1.9 and 5.3 nm, respectively). These metal NPs were used as catalysts in hydrogenation reactions of dicarboxylic acids in water at room pressure and temperature. The NPs catalysed the selective transformation of fumaric and malonic acids to succinic acid, although with different yields: the best results were obtained in presence of Pd and Rh NPs (80 and 100%). Carrying out the hydrogenations on muconic acids (also deriving from biomass), the formation of adipic acid, a key building-block in the polymer industry, was observed with all NPs but the full selectivity with Rh NPs was remarkable, considering the mild conditions.[6]

We will also show the preliminary results of the synthesis and characterization of Pd and Rh NPs, using sheep wool, an important waste, especially in Central and South Italy, and hydrogen-donor agents. Also these NPs were used as catalysts in the reduction of unsaturated dicarboxylic acids with excellent selectivities. In this case, the wool-support simplified the recover/reuse of the metal catalysts.

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P79

ONE-POT SYNTHESIS OF Zn-DOPED MESOPOROUS SILICA KCC-1

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Inorganic mesoporous silica nanoparticles have gained significant attention due to their exceptional properties and their potential applications in various fields, including catalysis, drug delivery, and sensing [1]. This study focuses on the one-pot synthesis of zinc-doped mesoporous silica KCC-1 nanoparticles using a zinc acetate precursor, providing an alternative approach to the zinc oxide-based methods[2]. By varying the concentration of the zinc acetate precursor, the dependence of nanoparticle morphology on the zinc concentration is investigated by Scanning Electron Microscopy analysis. This morphological dependence is of utmost importance as it can significantly influence the nanoparticles' physical and chemical properties, such as surface area, pore size, and drug loading capacity.To gain further insights into the chemical state of zinc within the silica matrix, X-ray Photoelectron Spectroscopy (XPS) is employed for comprehensive characterization. XPS analysis confirms the successful incorporation of zinc into the mesoporous silica KCC-1 nanoparticles and provides valuable information about its chemical state. The chemical state characterization elucidates the bonding configuration of zinc, thereby enabling a better understanding of its interactions within the silica framework. This information is crucial for tailoring the properties and performance of the zinc-doped nanoparticles for specific applications. In conclusion, the one-pot synthesis of zinc-doped mesoporous silica KCC-1 nanoparticles using zinc acetate as the precursor contributes to broader the understanding of zinc-doped mesoporous silica materials and pave the way for their application in diverse fields, ranging from biomedicine to environmental science.

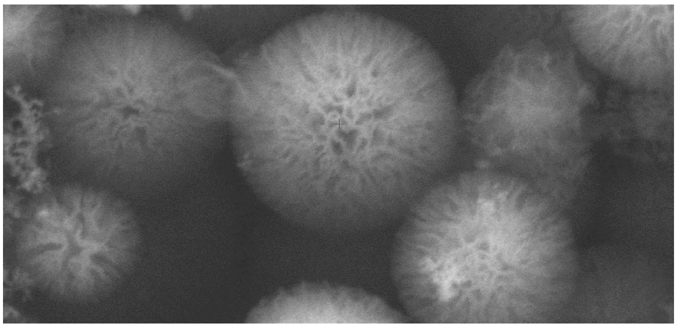

Figure 1*: SEM picture of KCC-1 nanoparticles doped with Zn*

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P80

HIGHLY ACTIVE Cp*-Ir CATALYSTS FOR CHEMICAL NADH REGENERATION

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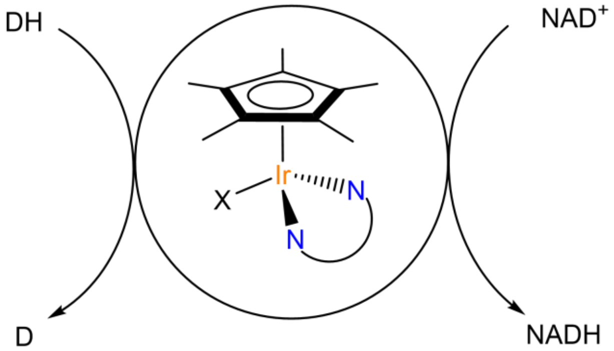
The NADH cofactor is a high-energy redox mediator successfully employed in many biological processes catalysed by oxidoreductase enzymes. Owing to its high cost, the regeneration of NADH starting from economical starting materials is highly desirable. Previous studies showed that Ir Cp* complexes can efficiently and selectively reduce NAD^+ to 1,4-NADH, the biologically active form, employing formate or phosphonic acid as hydride donors.[1,2,3]

In this contribution we will report the synthesis and complete characterization (in solution by multinuclear and multidimensional NMR spectroscopy and in the solid state through single-crystal X-Ray diffraction) of new Cp*Ir complexes, bearing N,N-type ancillary ligands, and their application to the hydrogenation of NAD^+ using formate and phosphonic acid (DH) as hydride donors (Figure 1). The novel catalysts lead to the regiospecific fromation1,4-NADH and showed unprecedented catalytic activity with TOF comparable or even exceeding that of enzymes.



DH = $HCOO^-$ or H_3PO_3

Figure 1. *Schematic rapresentation of the chemical NADH regenarion mediated by Cp*Ir catalysts.*

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P81

MANGANESE CARBONATE AS AN EFFICIENT ELECTROCATALYST FOR THECONVERSION OF AMMONIA (NH_4^+/NH_3) TO DINITROGEN

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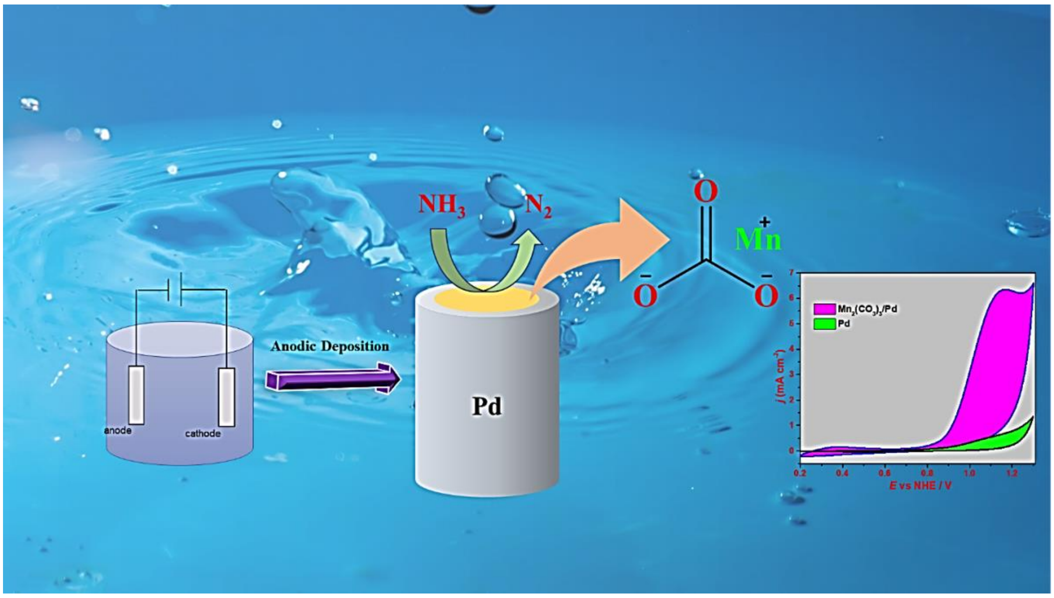
Energy generation from a sustainable renewable source is seen as an imperative tool to meet the energy demand of the present day. Moreover, obtaining clean energy fuel e.g., H_2 is the need of the hour and hence, oxidation of ammonia might be a solution to this milestone. $Mn_2(CO_3)_3$ deposited electrochemically on the surface of a Pd electrode is a good electrocatalyst for the oxidation of ammonia (AOR) to dinitrogen. The AOR occurs in solutions containing Na_2CO_3 and NH_4OH as electrolytes. The $Mn_2(CO_3)_3$/Pd electrode has a high electrocatalytic oxidation current density of 6.4 mA cm^{-2} at anodic potential of 1.16 V vs. NHE.Chronoamperometric experiments for the durability test is suggestive of $Mn_2(CO_3)_3$ being stable for 4 h towards ammonia oxidation reaction. Also, on careful investigation of the products formed upon oxidation of ammonia, only nitrogen as a product was observed.



P82

WELL-DEFINED AND “COMPLETE” Al-COCATALYSTS FOR OLEFIN POLYMERIZATION

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The performances of molecular catalysts for olefin polymerization, matched with ever-growing industrial applications especially in the copolymerization of ethene with higher 1-alkenes, are crucially dependent on the choice of the activator. Despite their fundamental role in precatalyst activation, cocatalysts have seen only limited advancements in the last decades.[1] Recently, we reported the discovery of a new Al-based cocatalyst, that is an unusual homodinuclear cationic species with two Al centers bridged by an hydride ($\{[iBu_2(PhMe_2N)Al]_2(\mu\text{-}H)\}^+[B(C_6F_5)_4]^-$, AlHAl, Figure 1).[2] This species combines the ability of acting as abstractor, alkylator, and scavenger like methylalumoxane (MAO) with a defined molecular structure typical of borate salt activators. The efficacy of the AlHAl as cocatalyst relies on the coordinately saturated Al-centers possessing “latent” Lewis acidity. As a matter of fact, AlHAl can be seen as a donor-stabilized $[AliBu_2]^+$ cation. This new co-catalyst is easily synthesizable, stable at room temperature, and amenable to structural variations; it can therefore be considered the prototype of a new class of activators.[3] In this respect, we are synthesizing and testing a variety of AlHAl analogues differing for the nature of the N-donor (L), aiming to tune the latent Lewis acidity and gain insights on the factors determining cocatalytic properties. The synthesis of AlHAl-L analogues will be discussed, also highlighting the unexpected side-reactivity observed in some cases, along with the performances of this new class of activators in olefin polymerization with various catalysts. In particular, results of a systematic screening in a parallel pressure reactor (PPR) high-throughput experiment (HTE) platform will be presented.

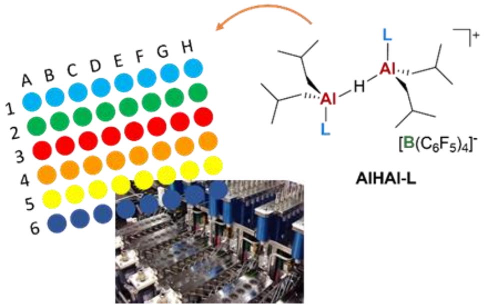

***Figure 1**: Schematic representation of a high-throughput screening at varying N-donor L.*

***Acknowledgements**: This research forms part of the DPI research program, project #857.*

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P83

FLUORESCENT GOLD NANOPARTICLES AS CARRIER FOR RADIOPHARMACEUTICALS

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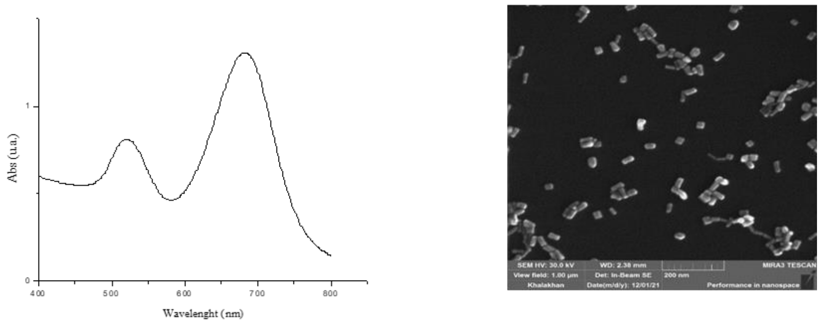
The functionalized gold nanorods (AuNRs) are catching a lot of attention in the biomedical field for their physical-chemical features, such as surface plasmon resonance (SPR), and the synthetic versatility [1-2]. In addition, the AuNRs can issue Auger Electrons (the low energy electrons, AEs) which are similar to those emitted by the decay of 99m technetium (^{99m}Tc), a radioactive nuclide widely used for diagnostic nuclear medicine [3]. Radiopharmaceuticals, used for diagnosis, could actually be used in theragnostic fields when loaded on AuNRs and delivered to the tumor target, exploiting the emission of extra AEs by rods [4]. In this work, it is presented a new drug delivery system with AuNRs conjugated with fluorescein isothiocyanate (FITC) and radiopharmaceutical based on ^{99}Tc-sestaMIBI (after 99mTc decay). Characterizations with DLS, FESEM-EDX and UV-VIS, FT-IR and SR-XPS spectroscopies, FT-R-XPS has allowed the study of the drug-AuNRs interactions (Figure 1). Furthermore, preliminary radiobiological data on the cellular killing of glioblastoma cells (T98G) are presented.



(a) ***(b)***

Figure 1*: AuNRs (a) Uv-vis spectrum in H_2O (λ_{max}= 520 - 680 nm); (b) FESEM image (39 ± 5 x 11 ± 2 nm)*

Acknowledgements**:** *Grant of Excellence Departments 2023-2027, MIUR (ARTICOLO 1, COMMI 314–337 LEGGE 232/2016) by authors from Roma Tre University. Prof. Venditti, Iucci and Battocchio thank the Rome Technopole Project CUP: F83B22000040006.*

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P84

SULFONATED N-HETEROCYCLIC CARBENE SILVER(I) AND GOLD(I) COMPLEXES IN π-FUNCTIONALIZATION OF ALKYNES

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Alkynes are versatile organic compounds due to their unsaturated bonds. These electron-rich bonds well fit oxidative processes and electrophilic additions. Alkynes can act as nucleophilic groups in their acetylide form and as electrophilic groups as well, although the latter are more challenging to handle without the use of metallic salts or organometallic complexes[1]. Transition metals like silver and gold have a strong affinity for alkynes. Acting as soft Lewis acid centers, they can coordinate unsaturated bonds, facilitating nucleophilic addition and the formation of acetylides in mild conditions[2,3]. Due to their applicability, the research for more suitable classes of ligands in these complexes is continuous, and N-heterocyclic carbene (NHC) ligands are particularly interesting. NHC ligands were first synthesized and characterized as stable carbenes by Arduengo[4]. These ligands are known for their versatility and stabilizing capacities in organometallic structures. As a result, Ag(I)- and Au(I)-NHC complexes have found wide applications in catalysis with alkyne substrates to promote attractive and more environmentally sustainable reactions. Our research aims to synthesize, characterize, and use in catalysis novel homoleptic sulfonated N-heterocyclic carbene silver(I) and gold(I) complexes (Figure 1):

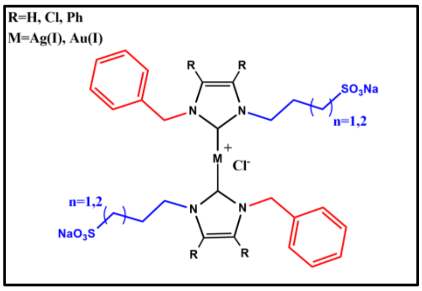

***Figure 1**: Homoleptic sulfonated N-heterocyclic carbene of silver(I) and gold(I) complexes*

The chosen reactions to test the metal complexes are: A^3-coupling reaction (alkynes, aldehydes, amines)[5], carboxylation of terminal alkynes[6] and synthesis of 2-oxazolidinones through cyclization of propargylamines[7].

***Acknowledgements*:**

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P85

STRUCTURAL PROPERTIES DETERMINING THE NEAR-EDGE X-RAY ABSORPTION SPECTRA OF LEAD HALIDE PEROVSKITES

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X-ray absorption spectroscopy (XAS) is an excellent complement to diffraction techniques for studying the structure of materials. Despite the extensive research on lead halide perovskites for optoelectronic applications, the application of XAS to these materials has been relatively limited and yielded varying degrees of success. In order to develop generalizable approaches for analyzing XAS spectra of halide perovskites with different compositions, we conducted an experimental and computational study on a hybrid Pb/Bi iodide solid solution, serving as a model system. The monodimensional lead halide "perovskite" $(TMSO)_3Pb_{3x}Bi_{2(1-x)}I_9$[1] exhibits correlated disorder at the metal cation site, resulting in various possible arrangements of Pb, Bi, and metal vacancies (Figure 1). Through simulations, we observed that the X-ray absorption near-edge structure spectra (at the Pb, Bi, and I X-ray absorption edges) show some sensitive to these alternations. Surprisingly, we discovered that the cation spectra can be explained by simple distortions of independent PbI_6/BiI_6 octahedral units, without considering long-range multiple scattering contributions that typically dominate the near-edge region.[2] This finding enables the prediction and modeling of X-ray absorption near-edge spectra using simple structural units, suggesting that similar approaches can be successfully extended to other halide perovskites in the future.

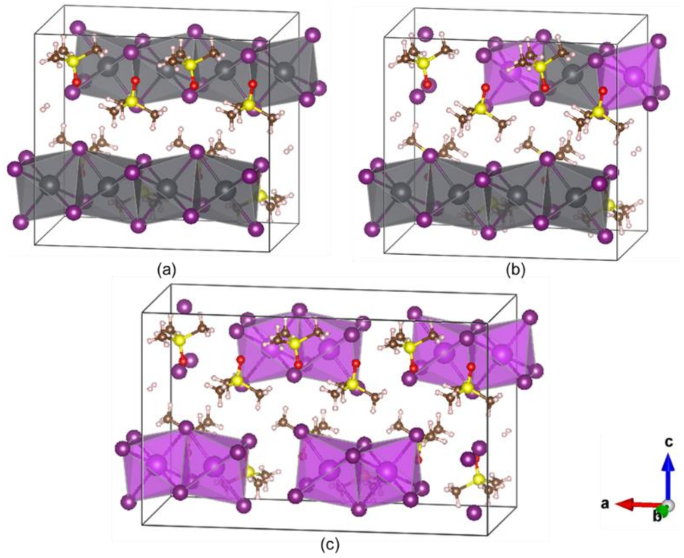

Figure 6*: (a) Undoped* $TMSO_8Pb_8I_{24}$ *2 x 1 x 1 supercell. (b) Pb/Bi iodide solid solution. (c)* $(TMSO)_3Bi_2I_9$*supercell.*

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P86

Cu AND Zn MOFs ARE EFFICIENT ANTIMICROBIAL MATERIALS IN THE PREVENTION OF POST-HARVEST DECAY OF CLIMACTERIC FRUITS ALONG THE SUPPLY CHAIN

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Microbial infections in agricultural production have a significant impact on world economy. It is estimated that food waste amount ~ 33–50% of global manufactured food spoils as consequence of microbial contamination during the storage/transport phases of supply chain. Metal-Organic Frameworks (MOFs) are emerging hybrid porous nanomaterials consisting of metal ions linked by organic binding ligands, possessing uniform structures with large-surface networks, good structural rigidity and tunable physical and chemical properties. They are attracting growing interest for antimicrobial applications due to their poor solubility in water and organic solvents, which allows their use in solid composite materials as antimicrobial additives. Here we report a detailed study of the antimicrobial activity of some previously reported Zn(II) and Cu(II) MOFs with bipyrazole linkers [1-3] against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacterial strains, as well as fungal strains *P. citrinum*, *P. expansum*, *C. gloeosporioides* and *M. piriformis* that typically attack climacteric fruits after harvesting. Mainly Zn-MOFs show a broad-spectrum activity and strong efficiency in inhibiting microbial growth, with a mechanism of action based on surface contact of MOFs nanoparticles with microbes through the so-called "chelation effect" and reactive oxygen species (ROS) generation [4].

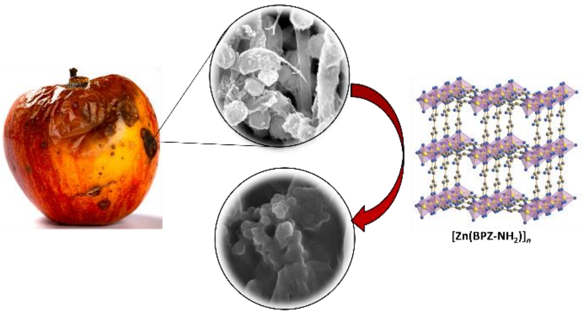

Figure 1*: Antifungal activity by* $[Zn(BPz\text{-}NH_2)]_n$ *showed through morphological changes in SEM images.*

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P87

TWO NOVEL WATER SOLUBLE LIGANDS FOR THE DESIGN OF METAL-BASED ANTICANCER DRUGS

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O, N and S donor ligands are interesting species in the field of coordination chemistry: among them, very little is known about thiocarbohydrazones (TCH) and carbohydrazones (CH), the higher homologues of the well-known thiosemicarbazones (TSC) and semicarbazones (SC), and their metal complexes [1]. TCHs and CHs are versatile molecules with several possible solution structures including configurational isomers around the imine bond and thione/thiol (or keto/enol) tautomers[2] and they can form monometallic and bimetallic (homo- and hetero-nuclear) complexes [1]. Taking in mind these features, we selected TCHs and CHs to be used as ligands towards metals of biological interest (Cu(II), Zn(II)) with the aim to develop novel anticancer metallodrugs.

Since water solubility is one of the critical parameters for the development of pharmaceuticals [3], we decided to introduce two sulfonate groups on the organic backbone of the ligands, in order to ensure solubility in physiological medium to the corresponding metal complexes.

A sulfonated bis-TCH (**1**) and a sulfonated bis-CH (**2**) (Fig. 1) were successfully synthesized and fully characterized. They proved to be highly soluble in water and sparingly soluble in ethanol at room temperature. In order to study the coordination properties of the ligands towards Cu^{2+} and Zn^{2+} metal ions, we performed a series of spectrophotometric UV-vis titrations in aqueous 25 mM HEPES buffer at pH 7.4,determining the species present in solution and the corresponding binding constants. Preliminary evaluation of the cytotoxic profile of both ligands and metal complexes is currently ongoing.

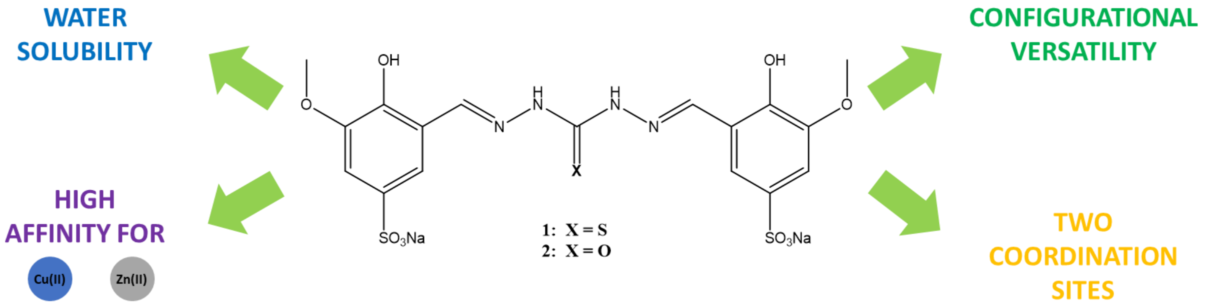

Figure 1: *Ligands* **1** *and* **2**: *molecular structure and chemical features.*

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P88

STRUCTURAL ANALYSIS, DYNAMICS AND REACTIVITY OF Zr AND Hf SALAN COMPLEXES

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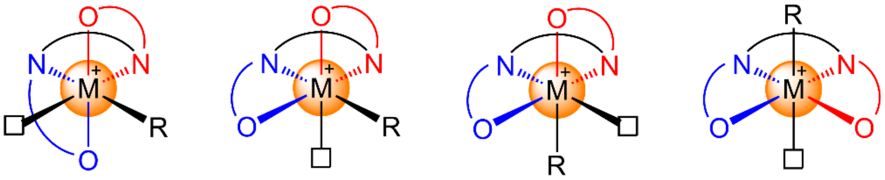
Coordinative vacancies play a crucial role in transition metal catalysis. This applies especially in olefin polymerization catalysed by Group 4 metal complexes, where the availability of vacant sites regulates monomer uptake and chain propagation.[1] Activated cationic Group 4 post-metallocene catalysts may speciate into various possible geometrical isomers (Figure 1), some of which may be dormant or inactive. Rationalizing how substituents on the ancillary ligand and solvent modulate the equilibria between isomers, and, consequently, catalytic performance, is challenging.



fac-fac fac-mer fac-mer mer-mer

***Figure 1**: possible isomers of active [ONNO]M-R$^+$species*

This contributionfocuses on selected Group 4 post-metallocene systems based on tetradentate [ONNO] ligand (Salan type)which display distinctly different polymerization productivities as a function of ligand scaffold.[2] An in-depth NMR investigation, applying a battery of homo and heteronuclear 1D and 2D NMR techniques, allowed to disclose the solution structure of the cationic precursors, [ONNO]M-Bn$^+$, which was shown to be critically dependent on ligand substituents and solvent (toluene and chlorobenzene). For the first time, solid-state structures of solvent-coordinated activated cationic complexes of this class were obtained, further supporting NMR findings in solution. NMR Dynamics and DFT studies elucidate the solvent role. Importantly, easily accessible and diagnostic ^{13}C-NMR chemical shift differences for the NMe atoms in different isomers uncovered for [ONNO]M-Bn$^+$ complexes allowed NMR identification of the predominant resting state isomer for [ONNO]M-Polymeryl$^+$ species under polymerization conditions.

***Acknowledgements**: This research forms part of the research programme of DPI, project #835*

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P89

PROSTATE CANCER AND HEAVY METALS

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Exposure to metals can significantly increase the risk of cancer development, especially in kidneys, bladder, liver, skin, lungs, and gastric district.[1] Arsenic, beryllium, cadmium, chromium and nickel have been classified as Group 1 carcinogens by the International Agency for Research on Cancer, but also other metals, such as aluminium, cobalt, lead and antimony, are suspected carcinogens or co-carcinogens. All these elements are able to induce DNA damage, ROS production, oxidative stress, and cell death processes, resulting in enhanced risk of cancer and cancer-related conditions.[2] The molecular mechanisms of metal-induced carcinogenesis include mutagenesis, genotoxicity, epigenetic modifications such as DNA methylation, alteration in microRNA regulation and histone post-translational modification, competition with essential metals and cancer-related signalling pathways.[3]

In order to verify whether one or more metals were involved in prostate neoplasia we have analysed via ICP-MS both serum and urine samples obtained from 87 patients, of which 48 had a prostate cancer diagnosis, 29 were healthy donors, and 10 suffered from benign prostatic hyperplasia, which were considered as borderline patients. ICP-MS elemental identification and quantification involved 14 metals including manganese, cobalt, vanadium, iron, copper, zinc, selenium, arsenic, molybdenum, cadmium, antimony, barium, mercury and lead.

Here we will report and discuss the results obtained in this study.

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COMPARATIVE STUDY FOR ELECTROCHEMICAL PERFORMANCE OF 2D MATERIALS: STRUCTURES, SYNTHESIS AND ELECTROCATALYTIC APPLICATIONS

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Efficient hydrogen production by water electrolysis is vital for the development of renewable energy. To overcome the present challenge, high-performance novel electrocatalysts are required to replace fossil fuel and accelerate the development of an efficient electrolysis technology. In water electrolysis, the sluggish oxygen evolution reaction (OER) in anode limits the overall water splitting rate. Therefore, electrocatalysts handling water splitting have been investigated to enhance electrolytic efficiency. In particular, the development of sufficiently available, low-cost, highly active OER electrocatalyst in alkaline medium is of high demand in the present scenario. Recently, extensive studies have been conducted on non-noble-metal-based OER electrocatalysts, such as oxides, hydroxides, sulfides, selenides, tellurides, phosphides, layered double hydroxides (LDH) and zirconium phosphates which could play a crucial role in the OER in alkaline medium. [1] Two-dimensional (2D) materials possess extensive influence on the applications as electrocatalysts because of the large surface area and tunable electronic properties which are favorable for exposing catalytic active sites and attractive for surface catalysis. In particular, transition metals such as Fe, Co and Ni and their derivatives are extensively used as effective electrocatalysts for OER in alkaline medium. To this end, this work attempted to compare different layered materials such as layered double hydroxides, zirconium phosphate and zirconium phosphonates which are able to support catalytic active metal ions and to understand the correlation between the layered structural characteristics and the catalytic performance.

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