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Metal-Containing Nanoparticles: Design and Reactivity

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Nanochemistry is at the cross-road of solid-state and molecular chemistry. Moreover, nanotechnology relies both on the core and surface properties of metal-containing nanoparticles. There is a need to design and study these objects with both aspects in mind, especially considering the high capability of matter to reorganize at this scale and the dynamics observed both for the inorganic part of the nanoparticles (the core, such as $\text{Cu}^{(0)}$,^[1] FeP , or $\text{Gd}_2\text{O}_2\text{S}^{[2]}$) and for their shell of organic ligands (oleates,^[3] alkylphosphines,^[4] *N*-heterocyclic carbenes,^[5] etc.).

It is with this “inside and out” mindset that I will discuss the recent developments on four families of nanoparticles: metal and alloys,^[6] metal carbides (using KC_8 as a carbon source),^[7] metal phosphides (using P_4 or a cyclophosphane)^[8] and metal oxysulfides. I will propose principles for a rationale design of new synthetic routes, in which the role of all reactants and their stoichiometry is controlled. I will emphasize how surface reactivity (eg. in the context of catalysis and electrocatalysis) influences the overall behavior of the nanoparticles.

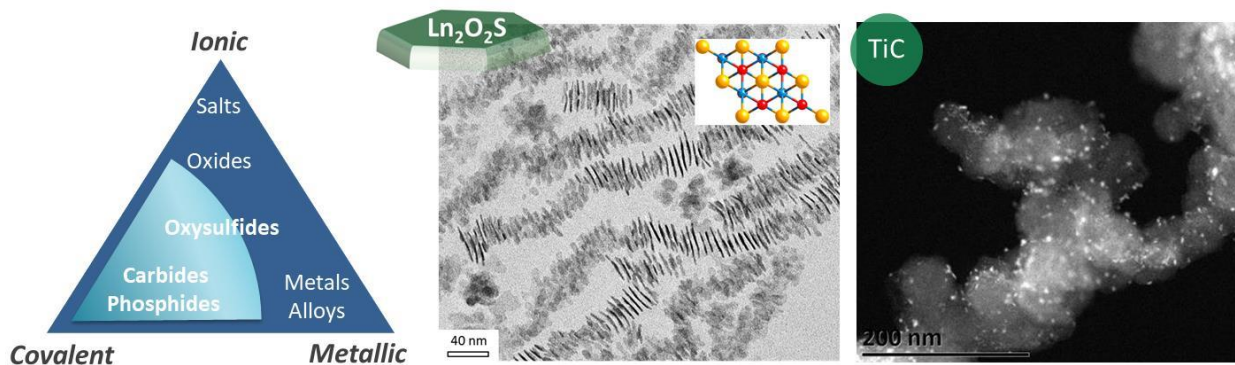


Figure 1 Van Arkel-Ketelaar triangle with the bonding situation of metal phosphides, carbides and oxysulfides. Lanthanide oxysulfide nanoplates and their crystalline structure.^[2] Titanium carbide nanoparticles supported on acetylene black, prepared in one step.^[7]

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Molecular upconversion with lanthanide complexes

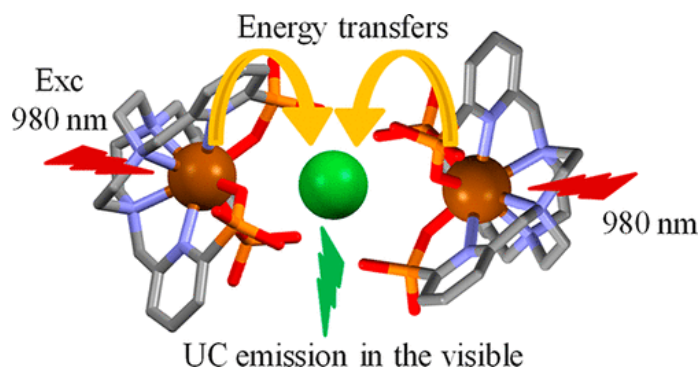
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Upconversion (UC) is a process which consists in piling up the energy of multiple photons in a material to obtain luminescence at a higher energy than the excitation source.¹ Applications of UC can be found in numerous fields such as anti-counterfeiting inks, photovoltaics or bioimaging.

Since the first observations of UC in the 1960s, this phenomenon has been mainly restricted to solid state materials and nanoparticles,² but the last decade has seen the emergence of discrete molecular entities exhibiting UC in solution, and few examples are now displaying compelling efficiencies, even in pure water.³



Principle of molecular UC in a heteropolynuclear [(YbL)₂Tb] complex³

After a brief recall of the basic principles of UC and of the challenges associated to molecular UC, we will examine the way the problem of molecular UC has been tackled in our team using coordination chemistry of luminescent lanthanide ions assembled by a supramolecular approach.

Equipe de Synthèse Pour l'Analyse (SynPA)

<http://www.iphc.cnrs.fr/SynPA>



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Towards Electron-triggered Coordination-induced Spin State Switching in Viologen-based Metal Complexes

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The control of magnetic properties by external stimuli has attracted much interest over the past few decades and tremendous work has been achieved thereafter.¹ Our contribution to this field is based on the coordination-induced spin state switching approach (CiSSS)² which, as its name implies, aims at changing the spin state of a metal center by modifying its coordination sphere. Therefore, based on our expertise in supramolecular chemistry and with the help of theoretical calculations, a well-suited model system was designed and eventually synthesized. In this presentation, the targeted tweezer-like molecule features a redox-responsive viologen-based hinge tethering a high affinity ligand to a magnetically active metal center. In agreement with the concept depicted below, the electrical stimulation of the hinge is expected to trigger a large amplitude molecular motion driven by the reversible intramolecular π -dimerization of the electrochemically-generated viologen cation radicals.^{3,4} This fully reversible back and forth self-locking process will enable to control the coordination/dissociation of the ligand to/from the metal center and, consequently, its spin state. The spin-state switching process will be discussed on the grounds of spectroscopic, electrochemical and spectro-electrochemical data supported by quantum calculations.

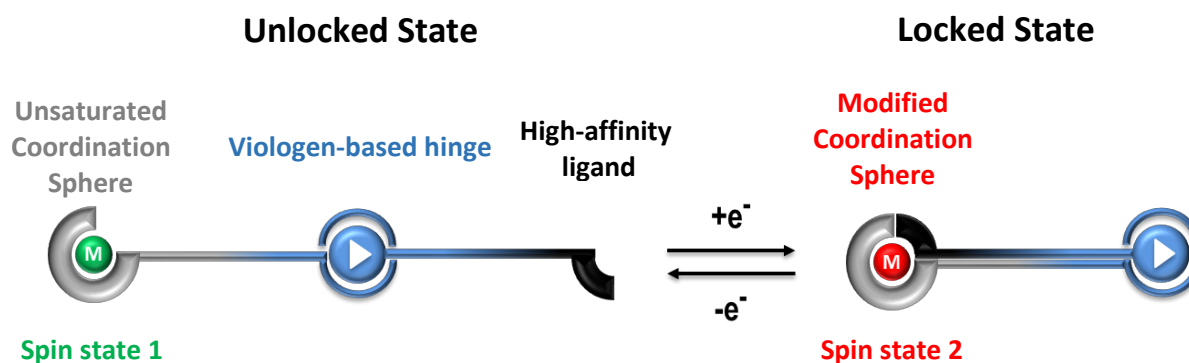


Figure 1 Electron-triggered self-locking behaviour for reversible CiSSS.

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Synthesis and characterization of chiral and chromophores based DTEs for the optical control of luminescence properties

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Luminescent molecules are present in a variety of domains, such as biology (bio-imaging), optoelectronics (data processing, molecular storage) or electroluminescent devices that are now part of our daily lives (OLED screens). In this highly competitive field, our approach aims to bring two additional dimensions. The first one is to control the luminescence by an external stimulus, here, light. Indeed, our research group has an expertise in the synthesis and study of the optical properties of photochromic luminescent molecules.^[1] The second dimension is to introduce chirality in these photochromic units in order to access light-switchable circularly polarized luminescence.^[2] This will pave the way for particularly promising multifunctional optical systems.

The introduction of chirality in dithienylethenes via atropoisomerism strategy was reached by blocking the interconversion between the two antiparallel forms and opens an opportunity for studying their chiroptical properties after separation of enantiomers.^[3] The introduction of a chromophore allowed the photocontrol of the circularly polarized luminescence property.

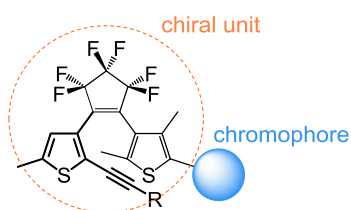


Figure 1 Design of the chiral DTEs

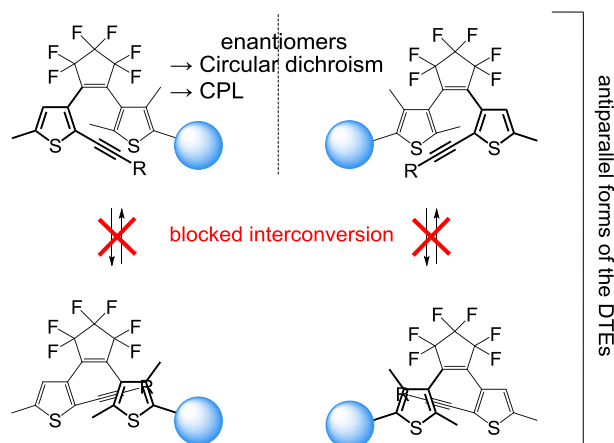


Figure 2 Blocked interconversion by atropoisomerism

The design strategy and the synthetic pathways, along with the optical properties of the synthesized molecules will be presented. The results of the following of the photochromism by ¹H and ¹⁹F NMR and UV-Visible absorption will be discussed. The dynamic of the system was also studied via variable temperature experiments.

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Cu(II)TMPA a colorimetric probe for fast detection of sulfite and thiosulfate ions

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Sodium sulfite (Na_2SO_3) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) are food additives with E numbers E221 and E539 respectively. They are used to preserve food, prevent browning and as anti-oxidant. The acceptable daily intake (ADI) is 0.7 mg per kg of body weight per person for both sodium sulfite and sodium thiosulfate.^{1,2} Sodium sulfite in large amount in food can be harmful, and causes asthmatic crises and allergic reactions to some people.¹ Therefore, it is important to be able to detect and estimate sulfite derivatives amount in foods and beverages.

Cu(II) complexes with Tren (tris(2-aminoethyl)amine) or Tren derivatives ligands already showed the ability to coordinate a thiosulfate ion.^{3,4} In our search for Cu(I)TMPA (TMPA = Tris(2-pyridylmethyl)amine) reactivity in aqueous medium (reduction of Cu(II)TMPA to Cu(I)TMPA under air by sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$)), we obtained TMPA-Cu(II) sulfite species and thus decided to fully characterized the interaction between TMPA-Cu(II) thiosulfate and sulfite (Figure 1).

The characterization of CuTMPA(SO_3) and CuTMPA(S_2O_3) complexes will be presented through X-ray crystallographic data, EPR, UV-Vis and electrochemistry signatures. Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ titrations would be shown. This technique was applied to sulfite detection in crystal sugar sample.

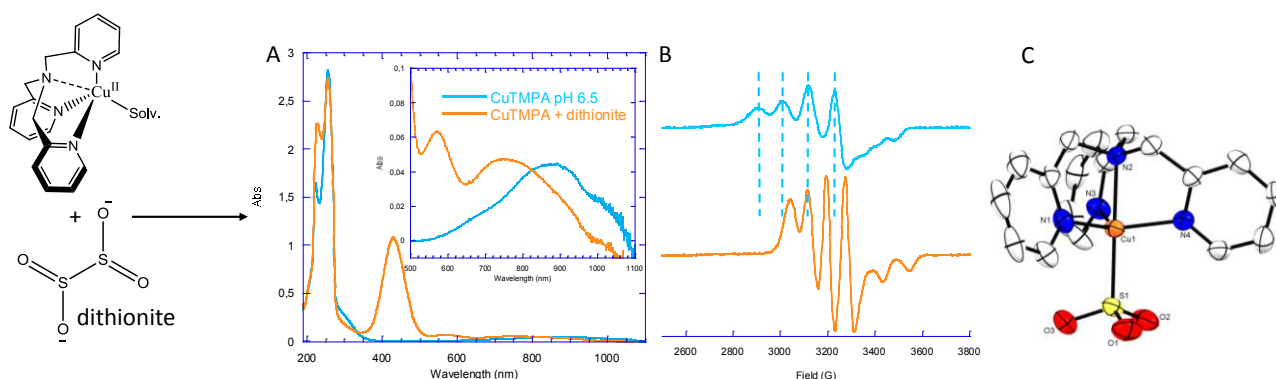


Figure 1 UV-vis spectra (A) and EPR spectra (B) of Cu(II)TMPA (blue) and Cu(II)TMPA after reaction with degradation product from sodium dithionite (orange). Conditions: [TMPA] = 0.22 mM; [Cu(II)SO₄·5H₂O] = 0.2 mM; [dithionite] = 1 mM; [HEPES] = 100 mM in aqueous phase in mixture of CH₃CN/HEPES pH 6.5 50/50. ORTEP view of the complex Cu(II)TMPA(SO₃) (hydrogens omitted for clarity).

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Molecular strategies for C–H activation using Cu(II) salts: towards the synthesis of imidazo[1,5-a]pyridines

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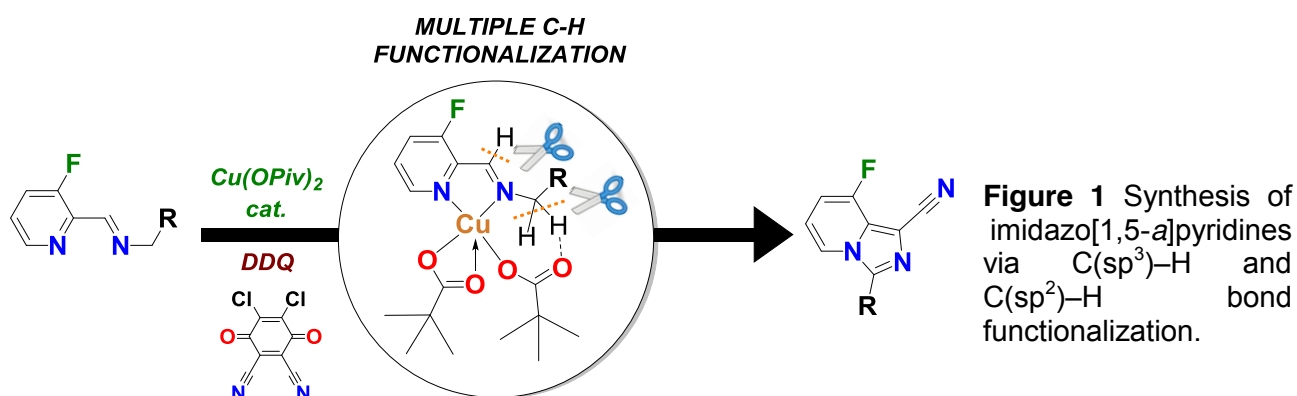
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The activation of C–H bonds has been for years a highly attractive topic in catalysis due to its convenience from a sustainable point of view, leading to a wide variety of valuable transformations. In particular, the functionalization of C(sp³)–H bonds in a selective and efficient manner is especially challenging, representing an attractive tool for the synthesis of targets exhibiting special interest in the Fine Chemistry sector.

Modern C–H activation makes a wide use of 4d transition metals, in particular Pd¹, as the key to access the functionalization of these robust bonds. But due to the scarcity of these precious metals, an increasing interest in the development of new pathways using earth-abundant metals has been growing since the beginning of XXI century².

In this work, the use of Cu(II) salts in the activation of C(sp³)–H bonds on picolyl imines as directing groups is studied, leading to the synthesis of imidazo[1,5-a]pyridines which are interesting synthetic targets for their pharmacological³ and photophysical properties⁴. This copper-catalyzed reaction works for a variety of substrates incorporating linear alkyl chains (from 3 to 12 carbon atoms) and good functional group tolerance (aryl, ether and ester groups). We have been interested in the identification of key intermediates in order to gain a better understanding of the reaction mechanism and explore the possibilities that this reactivity can offer.

This work adds new avenues towards multiple Cu-catalyzed C(sp³)–H and C(sp²)–H activation reactions towards the synthesis and functionalization of heterocycles.



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Stereoselective synthesis of NHC-Py Iron(II) complexes

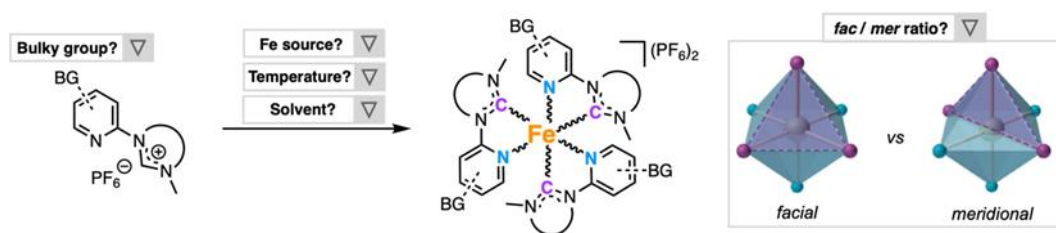
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Photoactive iron-based compounds as an alternative of expensive, rare and more toxic noble metals have received increasing interest in the last years.^[1] In fact, the judicious selection of ligands combining strong σ -donor and π -acceptor characters such as N-heterocyclic carbenes (NHC) mixed with pyridines allows to sufficiently destabilize the low-lying metal-centered excited states that typically lead to non-radiative deactivation to the ground state. As a result, complexes with relatively long-lived MLCT states have been successfully obtained and applied in fields like catalysis^[2] and, even more challenging, energy conversion.^[3]

Our research group has recently showed the beneficial effects on the optoelectronic properties of bidentate (**N²C**) over tridentate (**C¹N²C**) coordination for this type of NHC-py complexes.^[4,5] Competition of the two geometrical isomers *fac* and *mer* was also observed, with facial coordination being exclusively favored only when a C_3 -tripodal ligand was selected.^[4] However, although both isomers are well-known to exhibit distinct photophysical properties,^[4,6] a clear and selective protocol to get a single isomer with iron complexes was still missing.

Herein, we report on the influence of factors such as temperature or the nature of the iron source on the stereoselectivity of the complexation reaction [**Scheme 1**]. More importantly, we show the remarkably effect of the steric hindrance of the ligand in favoring one over the other isomer, even in an exclusive manner in some cases. For all complexes, properties are assessed mainly by means of UV-Vis absorption and electrochemistry.



Scheme 1

References:

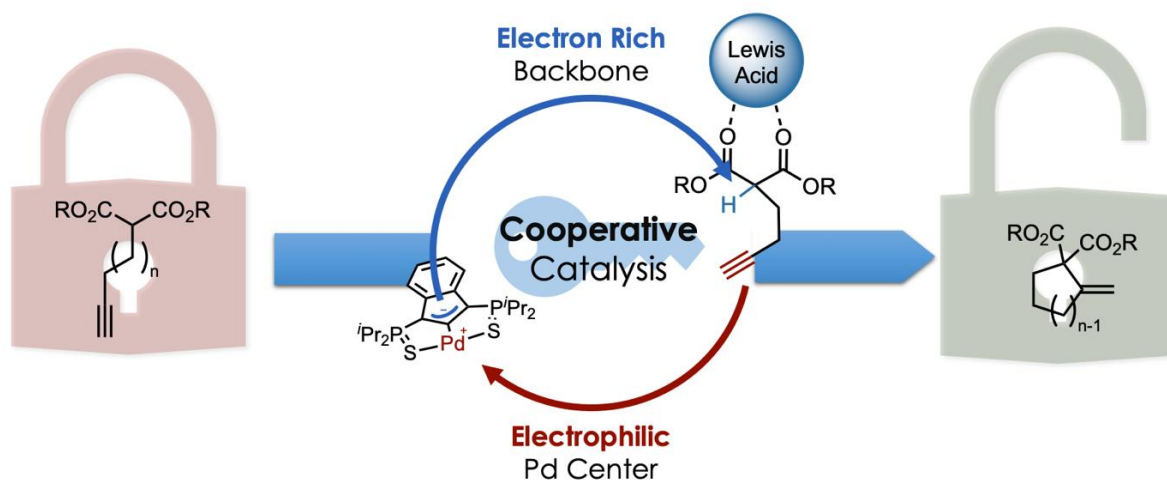
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Pd indenediide complex and Lewis acids additives: A double cooperative catalytic system applied to C-C bond formation

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Discovered by Le Perchec and Conia¹ in 1975, the eponym Conia-ene reaction has seen multiple advances. The early versions required high-temperatures and harsh conditions, decreasing the synthetic usefulness and interest for this reaction. The emergence of catalytic versions in the last 15 years² brought it back as a powerful tool for C-C bond formation. However, some limitations still need to be addressed, one of them being the lack of a unique versatile system with a broad substrate scope.

In this context, we have recently reported an efficient indenediide Pd^{II} pincer complex for the formation of C-O³ and C-N⁴ bonds in absence of external base thanks to the chemical non-innocent character of the indenediide ligand. These results prompted us to go one step-further, focusing on the formation of C-C bonds via a Conia-Ene cyclisation.



Thanks to the addition of Mg^{II} salt as Lewis acid, this multi-cooperative system was applied to the cycloisomerization of a wide variety of substrates including classical challenging ones. Interestingly, with internal alkynes our system promoted the more sterically demanding Z-alkene in contrast to reported catalysts in the literature. The robustness of this system was also evaluated as catalytic activity was retained with technical grade reagents under air.⁵

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Ligand-Driven Light Switching of Single Molecule Magnets

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Single Molecule Magnets offer unique features that may allow information to be stored with much higher densities, and to be processed at unprecedented speeds. [1] In order to use SMM in information storage devices, it would be a great advantage to control the magnetic properties by applying external stimuli. Light is fascinating in this purpose due to its easy and contactless application, and sustainability. [2]

The goal of our project is to create an efficient strategy to switch reversibly the molecular magnetic behavior with light, relying on the photochromic abilities of a ligand, and on the recognized influence of the coordination environment on the SMM property. For this purpose, two different photochromic ligands with different coordinating abilities were chosen.

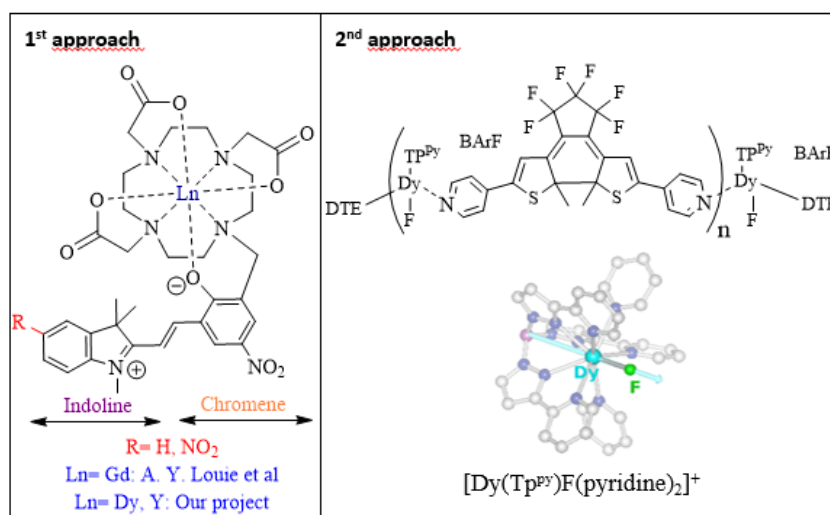


Figure 1 Designs of two approaches towards photo-switchable single molecule magnets

In our work, we incorporated photochromic ligands: spiropyrans (1st approach) [3],[4] and dithienylethenes (2nd approach) [5] into Dysprosium (III) based complexes in which photoisomerization can induce enough changes in the coordination environment and hence affect the electronic structure and relaxation behavior. In this presentation, we will present the synthesis of several macrocyclic photochromic complexes and DTE based complexes, and discuss the influence of different parameters on the stability of isomers.

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Ratiometric Ln³⁺-Based Luminescent Thermometers

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Temperature is a key parameter of many natural and artificial systems. Although several readout methods have been developed through time, nowadays technologies increased the demand to develop new methods with high precision down to the micro and nano scales. In this respect, luminescent thermometers have been emerged in the studies showing high sensitivity, spatial resolution, fast response, in addition of being non-invasive. Among this family, Ln³⁺-based luminescent thermometers take a great interest due to the unique photophysical properties of lanthanides originated from the shielded f orbitals⁽¹⁾.

We will present the first results of our work on the design of ratiometric Ln³⁺-based luminescent thermometers with performance based on following the variation in the intensity ratio of two Ln³⁺ emitting centers (Eu³⁺ and Tb³⁺). The transfers of energy in between both emitting species were controlled, thanks to the appropriate design of the ligand regarding the different excited states involved in the process⁽²⁾. These thermometers have a simple and easy processibility compared to previously reported systems, prepared by simply mixing complexes of the two Ln³⁺ centers. In addition, these thermometers show a promising performance as temperature sensors in the physiological range (293-323 K) making them possible candidates for future intracellular mapping of temperature, a parameter affecting the biological processes.

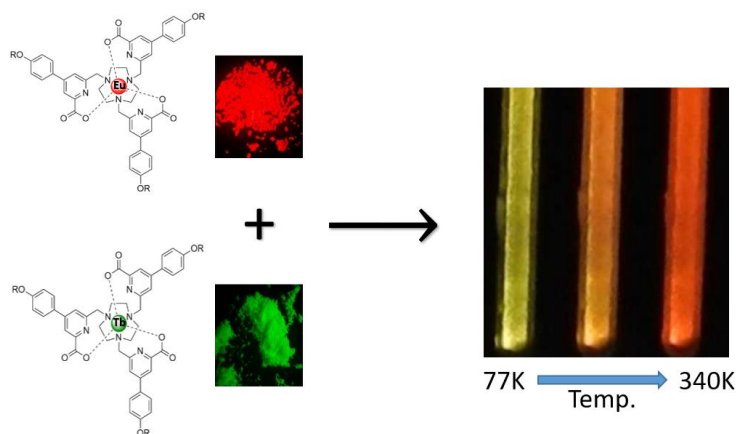


Figure 1 : Color changes (under UV light 365 nm) of Eu³⁺ and Tb³⁺ complexes mixture upon heating.

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Design of SMM via post-modification routes

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In the race of miniaturization and evolution of magnetic memories, the single-molecule magnets (SMM) are now a convincing alternative in data storage field as they act at the molecule level unlike the classical magnets. SMM are usually isolated complexes located elaborated by coordination chemistry routes. Their magnetic properties are based on axial magnetic anisotropy that creates a potential barrier (U_{eff}) separating two orientations of the magnetic moment and which depends on D (anisotropy) and S (total spin) of the molecular object ($U_{\text{eff}}=|D|S^2$). The first SMM, the $[\text{Mn}_{12}]$ one, was reported in 1980^[1] and magnetically characterized later in 1993.^[2] Ten years after, the first lanthanide-based SMM was reported.^[3] These $4f$ -based complexes are nowadays the most popular as the amplitude of the magnetic anisotropy (D) of some of the lanthanide trivalent cations is much stronger.

Previous studies^[4] at our laboratory have demonstrated that the nuclearity of the complex and the number of ligands coordinated to the metal center can be easily controlled by chemical routes and have a great impact on SMM's magnetic properties. As a conclusion, it appears that the simplest complex, mononuclear ones, show the most interesting SMM behavior and that the U_{eff} barrier can be finely controlled. Based on these results, our work consists now to design multifunctional SMM complex using a controlled manner. The idea is to be able to rationally design SMM molecular objects by associating lanthanide complexes with interesting properties using post-modification route of their organic moieties (organic chemistry reaction on $4f$ -based complexes). This strategy should allow to improve SMM performances and/or add a further functionality (luminescence, redox, ...) of the final material.

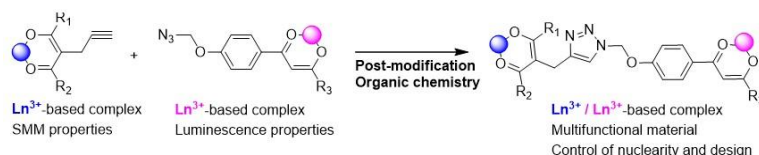


Figure 1: Principe of the post-modification in order to obtain multifunctional material using a controlled route

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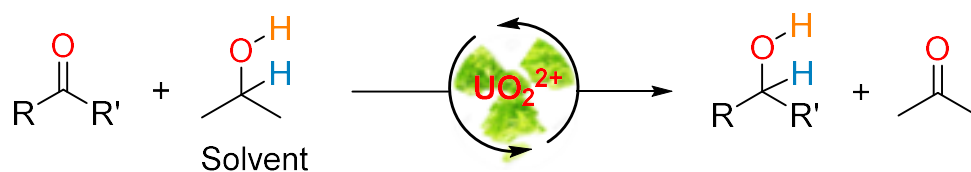
Uranyl(VI) Triflate as Catalyst for the Meerwein-Ponndorf-Verley reaction

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The selective reduction of carbonyl compounds is of particular importance in organic chemistry at both fundamental and industrial levels. Most often, strongly reactive metal hydrides (LiAlH₄ or NaBH₄) are used as stoichiometric reducing agents but catalytic reductions of substrates by direct hydrogenation or hydrogen atom transfer reactions from non-H₂ hydrogen sources (alcohol, formic acid) proved powerful alternative methods. Since the 1960's, innovative developments in molecular chemistry with metal catalysts (groups 8-11 metals in particular Ir, Ru, Rh) induced a craze in hydrogen transfer particularly within concepts of green chemistry developed in the 90's.¹ Nonetheless, high prices, toxicity and scarcity of the catalysts requires the use of more available elements of the periodic table.

The Meerwein-Ponndorf-Verley (MPV) reaction is an appealing route whereby aldehydes and ketones are reduced into the corresponding alcohols with an alcohol. Since 1925, when MPV reduction was first revealed with stoichiometric amounts of aluminum alkoxide as a promoter,^{2,3} more efficient agents and catalysts have been reported.⁴ Among them, strongly oxophilic trivalent f-elements were found catalytically active despite a high M–oxygen dissociation bond energy (BDE) that might have prevented efficient catalytic turnover. With the actinides, a pioneering work in 2000, revealed the ability of plutonium(III) isopropoxide (Pu(OⁱPr)₃) to act as a catalyst for the MPV reduction of ketones in ⁱPrOH while the U³⁺ and An⁴⁺ (An = U, Th) analogues were found inactive.⁵ Recently we reported the first reductive transformation of carbonyl molecules with hydrosilanes using the uranyl ion {UO₂}²⁺ as catalyst.⁶ The reaction was however limited to aldehydes. In this study we considered UO₂(OTf)₂ as a catalyst in the Meerwein-Ponndorf-Verley reduction for a number of aromatic and aliphatic aldehydes and ketones.



R = aryl, alkyl; R' = H, aryl, alkyl

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Probing the electrochemical reductive activation of O₂ catalyzed by Fe porphyrins using scanning electrochemical microscopy

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Oxidation of hydrocarbons are reactions of great importance for the preparation of various organic molecules in an industrial scale. Hazardous chemical agents and/or noble metal catalysts are often necessary in these processes because O₂, despite its potent oxidizing power, is kinetically inert preventing it from reacting in ambient conditions.^[1]

Metalloenzymes such as CytP450 whose active site contains a heme moiety, carry out highly efficient and selective oxidations under physiological conditions throughout the reductive activation of O₂. The latter consists of the partial and controlled reduction of O₂ bound at the metal active site *via* sequential e⁻ and H⁺ transfers to achieve O-O bond cleavage and generate the reactive high valent Fe-oxo (FeO) species.^[2] Chemically prepared intermediates such as Fe-superoxo (FeOO^{•-}), Fe-peroxo (FeOO²⁻), Fe-hydroperoxo (FeOOH⁻) as well as Fe-oxo (FeO) of Fe porphyrin complexes (models of the enzymes active site) have been characterized and the latter have been shown to be able to oxidize substrates.^[3] Using the electrochemical approach, which can circumvent the need for chemical oxidants because the necessary electrons are provided heterogeneously by an electrode, our group has previously evidenced the electrochemical formation of the Fe^{III}OO²⁻ and Fe^{III}OOH⁻ and Fe^{IV}O from a starting Fe^{III} and O₂.^[4]

Here we present the first example of using scanning electrochemical microscopy (SECM) to quantitatively analyse O₂ reductive activation in organic media catalysed by three different Fe porphyrins. For each porphyrin, SECM can provide in one single experiment the redox potential of various intermediates, and by fitting the obtained curves with simulated ones, the association constant of Fe^{II} with O₂, and the dissociation constant of the Fe^{III}OO²⁻ (peroxo) complex. The results obtained can contribute to a further understanding of the parameters controlling the catalytic efficiency of the Fe porphyrin towards O₂ activation and reduction.^[5]

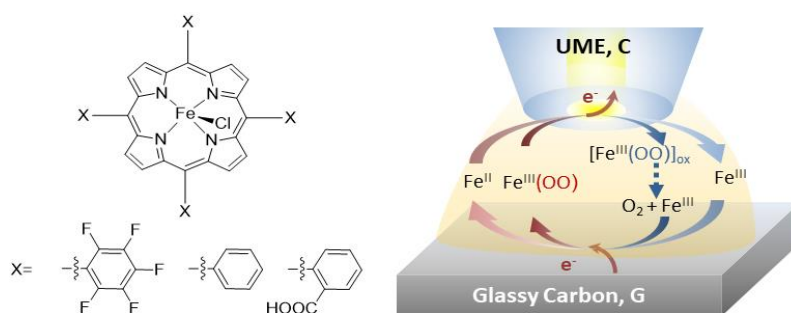


Figure 1. Left: [Fe^{III}(F₂₀TPP)Cl], [Fe^{III}(TPP)Cl], [Fe^{III}((2-CO₂H)₄TPP)Cl]; Right: Set-up used for a typical SECM–CV investigation for O₂ activation by Fe porphyrins. TPP= tetraphenylporphyrin.

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Photo/Electro-Induced Irreversible Isomerization of 2,2'-Azobispyridine Ligand in Arene Ruthenium(II)

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Azopyridine is a well-known photochromic organic compound that can act as ligand for metal center.¹ Linear patterns such as **I** and **II** are most common for 4,4'- and 3-3'-azobispyridine while bidentate or tridentate coordination mode with 5-membered chelate rings such as **IIIa** or **IIIb**, are found with *E*-2,2'-azobispyridine (Figure 1, left). A peculiar property of the latter ligand in these systems is that it usually does not undergo *E-Z* photo-isomerization. To the best of our knowledge, metal complexes of type **IV** involving coordination of the two nitrogen atoms of the pyridine rings of *Z*-2,2'-azobispyridine, suggested by Baldwin as early as 1969, have never been reported so far.²

In this work, we report the synthesis of novel arene Ru(II) complexes derived from 2,2'-azobispyridine, notably exhibiting an unprecedented *Z*-configured 7-membered chelate ring with the metal center. Their behavior in response to light or electrons will be detailed with absorption spectroscopy, electrochemistry, NMR spectroscopy, DFT calculations and X-Ray diffraction studies. (Figure 1, right).³

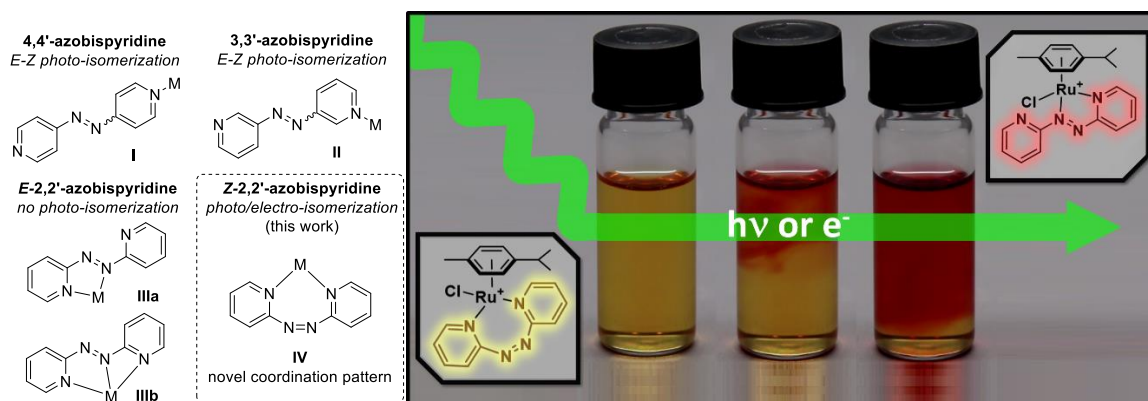


Figure 1 Left: Common coordination pattern exhibited by azobispyridine (**I**, **II**, **III**) and a novel 7-membered chelate ring described in the present study (**IV**). Right: Photo/Electro-induced irreversible isomerization of Ru complexes bearing 2,2'-azobispyridine ligand with concomitant rearrangement of the coordination pattern of the ligand.

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2-phenylbenzimidazole-based Ir(III) cationic complexes: solution and solid-state emission tuning through substitution of benzimidazole moiety.

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Phosphorescent materials such as cationic Ir(III) complexes have awakened a growing interest since their application in OLEDs, promoting the investment of millions of dollars in the development of these resources by the consumer electronic industry.¹ This is also encouraged by the possibility of using these cationic Ir(III) complexes in light-emitting electrochemical cells (LECs).²⁻⁴ Most of the Ir(III) complexes are phenylpyridine (ppy) based and research is focused on the tuning of the emission energy through modification of the ppy ligand.⁵ However Ir(III) complexes based on 2-phenylbenzimidazole are stimulating interest as neutral dopants in emitting devices since they offer multiple options to be tuned.⁶ Our group designed and synthesized new substituted 2-phenylbenzimidazole (pbi) ligands for a new family of pbi-based Ir(III) complexes in order to study the effect of different kinds of groups over the benzimidazole moiety on the photophysical and electrochemical properties. The benchmark complex of this new family displays similar photophysical properties in comparison with the model complex [Ir(ppy)₂(dmp)]PF₆ with $\Phi_{\text{PL}} = 20\%$ and 23% ⁵ respectively in degassed MeCN. The benchmark complex displays an improvement in the solid-state $\Phi_{\text{PL}} = 40\%$ for the neat solid in contrast with [Ir(ppy)₂(dmp)]BF₄ that achieve a $\Phi_{\text{PL}} = 19\%$ as neat film,⁷ among other interesting photophysical properties Figure 1.

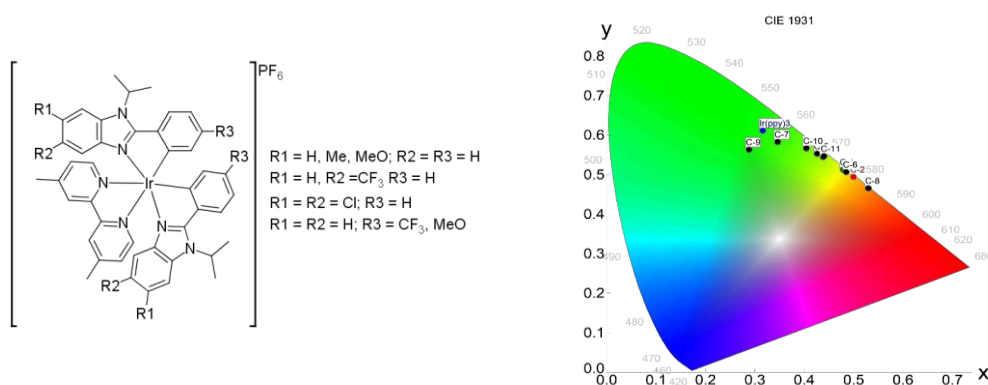


Figure 1. Structure and colour of emission of 2-phenylbenzimidazole based Ir(III) complexes in CH₂Cl₂.

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Design of new luminescent dye-doped silica nanoparticles using Cu(I) Complex photosensitizers

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The well-being of modern society leads to an increase of population and consequently to an increase of demand for pollutant and contaminant-free tap water. Ironically, with the increase of population comes the increase of both the number and the concentration of emerging organic pollutants (personal care products, drugs, pesticides...) and performant systems to detect them in water samples are required¹. In this frame, our goal consists in designing dye doped silica nanoparticles luminescent probes (**DDSNPs**), which could detect the presence of pollutants. These luminescent sensors¹ are made up of a silica shell which hosts luminescent dyes. These nano- objects show high brightness and are essentially benign. Many DDSNPs probes based on famous ruthenium complex $\text{Ru}(\text{bpy})_3^{2+}$ have been used. Yet, ruthenium is expensive and toxic and would be advantageously replaced by homoleptic Copper (I) complexes of the general formula $\text{Cu}(\text{NN})_2^+$ (where NN is a phenanthroline ligand bearing bulky groups in positions 2 and 9) (fig 1).

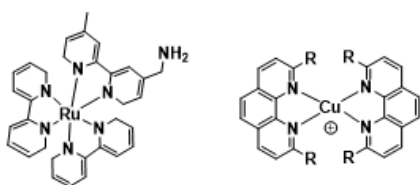


Fig.1: Ruthenium (II) Complex and Copper(I) Complex $\text{Cu}(\text{NN})_2^+$

In this contribution, we report our strategy to synthesize the first $\text{Cu}(\text{NN})_2^+$ doped silica nanoparticles as luminescent probes. This strategy relies on the design of a series of phenanthroline dyes with pending alkoxy silane functions that will be hydrolyzed with a silica molecular precursor (e.g.tetraethoxysilane) yielding the desired **DDSNPs**. The formation of these nanoparticles can be performed by the two main synthesis pathways: normal microemulsion² (path **A**) and reverse- microemulsion³ (path **B**). We performed the **B** syntheses and fully characterized the obtained nano-objects from a morphological point of view (TEM, DLS, ICP-AES) and physical point of view (optical properties). Compared to the free-molecular dye in water, suspensions of **DDSNPs** show dramatically enhanced stability and photophysical parameters.

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Development of functionalized resins for the purification of innovative radiopharmaceuticals

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Vector-driven internal radiotherapy is a rapidly growing field that completes the conventional techniques for cancer treatment such as surgery, chemotherapy or external radiotherapy. The appropriate radionuclide is coupled with a specific vector (monoclonal antibody, peptide...) in order to deliver the radioactivity specifically to the tumor cells. Contrary to the other methods, radioimmunotherapy allows the treatment of diffuse or metastatic tumors, limiting damage on the healthy tissues. Recent developments in isotope production now provide access to novel radionuclides and open new opportunities for theranostics. However, the production of novel radiopharmaceuticals is often limited by a short half-life (few days), high specific activities (> GBq/g) and high levels of isotopic purity required (> 99.9 %). Therefore, reliable and efficient separation and purification processes are needed. Solid phase extraction processes are an attractive solution for the purification of radionuclides, as they allow using simple, compact equipment, with obvious advantages for radioprotection and handling. Moreover, this type of processes produces less waste and effluents compared to solvent-type extraction and are largely operated using remote control.

An isotope of ruthenium has been selected for the development of a new radiopharmaceutical, in agreement with several criteria established by physicians, radiochemists, and nuclear engineers. Ruthenium can be produced from an irradiated metallic target. After dissolution of the irradiated material in nitric acid, ruthenium can be extracted and purified by solid phase extraction using a series of organic resins, either commercially available or specifically developed for this application. Results concerning the performance of the various resins in surrogate solutions will be presented and discussed. The present studies pave the way to the development of a novel ruthenium separation processes and contribute to a better understanding of the factors influencing the extraction properties of ruthenium isotopes.

Lanthanide complexes with ligand centered redox-activity: a redox active luminescent and magnetic switch

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The mapping of biological redox environment has gained increasing interest in recent years[1]. The development of bimodal probes that enable detection of redox state using medical imaging techniques is a fascinating topic of research. By combining them, it is possible to correlate the high sensitivity of luminescence and the high resolution of MRI for biological process. Lanthanide ions in medical imaging are well known due to their magnetic and photophysical properties, which have been unexploited as redox probes due to their propensity to remain in the +III state. By incorporating a redox active unit into the ligand, we targeted the detection of the oxidative stress which is involved in diverse pathologies as cancer or neurodegenerative diseases[2-3]. We previously reported a series of ligands based on redox active derivatives, which show specific responses in the luminescence and magnetic properties of the LnIII upon changes in the oxidation status[4] or in the presence of reactive oxygen species[5]. We now report on novel CEST active complexes which have been studied by electrochemistry, EPR, fluorescence spectroscopy, relaxivity and CEST techniques. Relaxivity and water exchange properties can be modulated by redox state and the coordination sphere around the metal

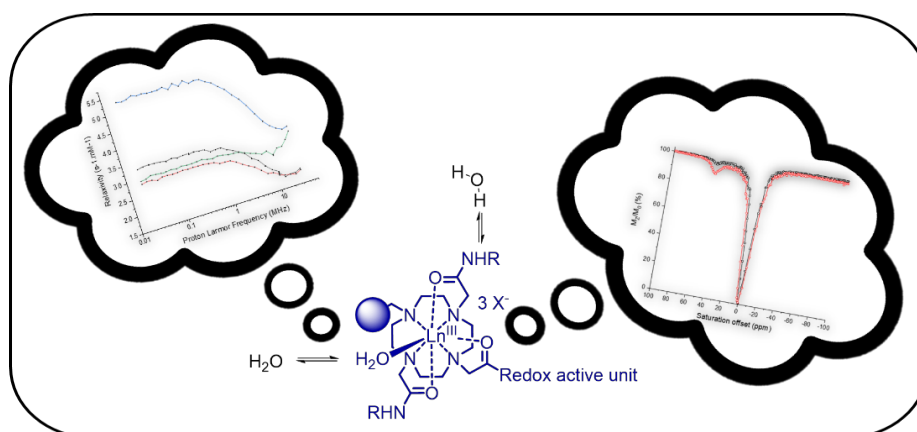


Figure 1 EPR and CEST redox switch

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Potential of amidinate gallium complexes as precursors for atomic layer deposition

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Atomic Layer Deposition (ALD) is a booming technology to deposit thin films and has been applied in several fields. This technique is based on surface-chemical reactions, and relies on the gas phase transport of metal containing molecules into a reaction chamber. However, not any molecule is suitable to be used as precursor, as they must be thermally robust while being sufficiently volatile and chemically labile to react with the surface functional groups. Organometallic chemistry offers an infinite set of options to design new efficient precursors, though predicting their volatility and reactivity in the ALD chamber remains tricky.¹

The target ligands are amidinate, as these are known for their relative ease of synthesis and their thermal stability. Amidinate-based complexes of tantalum, titanium and lanthanides have been tested as ALD precursors.²

This communication focuses on the development of new efficient amidinate gallium precursors to be used in the ALD of oxygen-free gallium-containing sulphide thin films.³ A series of gallium amidinate complexes were synthesized by tuning the substituents on both the endocyclic carbon atom of the ligand backbone and the ones on the nitrogen atoms, or by inserting alkyl or halide ligands in the coordination sphere of the gallium center, via a procedure similar to the one reported by Dagorne *et al.*⁴ To assess the thermal stability of the reagents and shed light on their transport in ALD, thermogravimetric analysis were realized under N₂ and vacuum to mimic transport conditions.

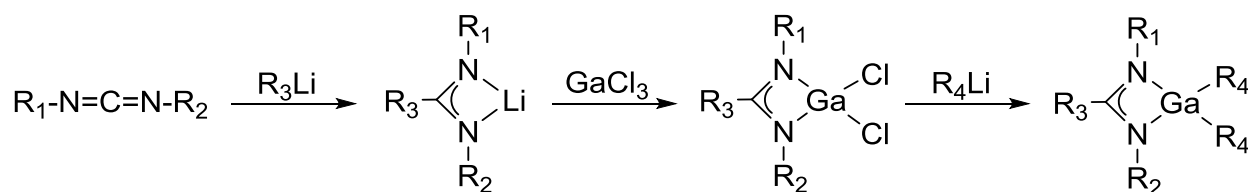


Figure 1 Developed procedure to access new amidinate gallium complex precursors (R₁, R₂ = Et, iPr, tBu; R₃ = Me, tBu, nBu, sBu; R₄ = Me)

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Nickel Alkoxide Complexes: Synthesis and Reactivity

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Late transition metal alkoxides are typically reactive species. This is rationalized by a four electron-two orbitals interaction between a lone pair at O and a filled orbital at the metal, which raises the energy of the molecular orbital mostly developed at the metal center. Among them, Nickel alkoxide complexes have shown to promote several reactions, such as copolymerization of CO₂ and epoxide,^[1] and proposed to be intermediates in others.^[2] Accordingly, very few examples of nickel alkoxide have been reported so far.^[3] It was our goal to develop a straightforward approach to a "Ni(OR)₂" fragment that would allow simple access to: a) a range of [(L)₂Ni(OR)₂] or [(L₂)Ni(OR)₂] complexes via ligand substitution/coordination; b) reactive "Ni(OR)⁺" metal fragment. We therefore selected and developed a synthesis of nickel complex **1** (fig. 1).

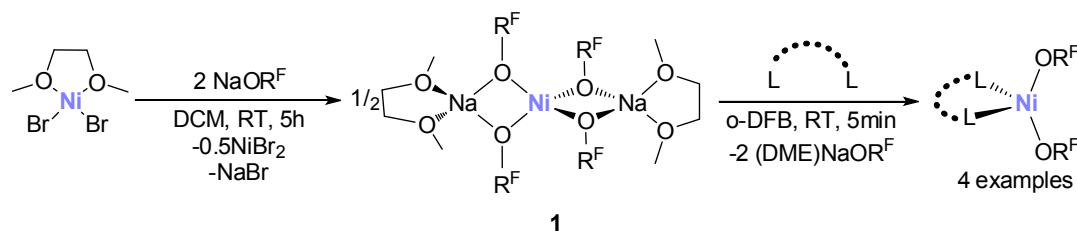


Figure 1 Synthesis of a new nickel alkoxide family. R^F=C(CF₃)₃.

As expected, in light of the poor coordinating capability of (DME)NaOR^F, the simple addition of monodentate or bidentate ligands yielded the desired complexes in excellent yields under very mild conditions.

In a second stage, the abstraction of one R^FO⁻ ligand from the coordination sphere was studied, in order to favor reactivity at the Ni center. Extensive DFT studies have allowed us to identify the (SⁱPr₂)Al(OR^F)₃ Lewis acid **3** as the optimal abstractor.

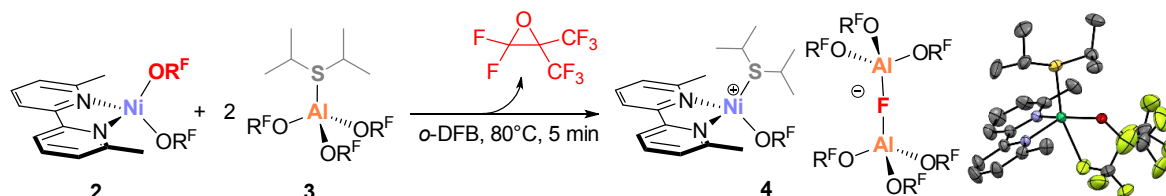


Figure 2 Cationization of **2** with (SⁱPr₂)Al(OR^F)₃. R^F=C(CF₃)₃.

Our results combining experimental and theoretical studies will be presented.

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In vivo albumin-binding of a cyclam-based platform for ^{64}Cu -PET imaging of cancers

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Radiometals are of great interest in the field of nuclear medicine particularly for PET imaging (Positron Emission Tomography) of numerous pathologies. Copper-64, as a β^+ emitter, is widely studied thanks to its half-life ($t=12.7\text{h}$) which is suitable for biological applications. In addition, this metal forms a theranostic pair with the β^- emitter ^{67}Cu , useful for cancer therapy. *N*-functionalized cyclam derivatives are very efficient chelating agents for Cu(II) complexation. Our group has developed a picolinate-cyclam, TE1PA, which forms a particularly stable and inert complex with Cu(II), avoiding the risks of dissociation or reduction in biological media.¹ In collaboration with the South African company NECSA specialized in the production of radioisotopes, we have synthesized a series of trifunctional cyclam-based chelating agents for ^{64}Cu -PET imaging of cancers called GluCAB for Glucose-Chelator-Albumin Bioconjugate.^{2,3} The pro-conjugate currently under investigations is composed of *i*) a TE1PA-based chelating agent for copper coordination, *ii*) a maleimide group for an *in vivo* albumin-binding that generates a passive targeting *via* the EPR (Enhanced Permeability and Retention) effect,⁴ and *iii*) a glucose unit for an active targeting to refine selectivity for a better accumulation of the radiopharmaceutical in tumor cells (**Figure 1**).

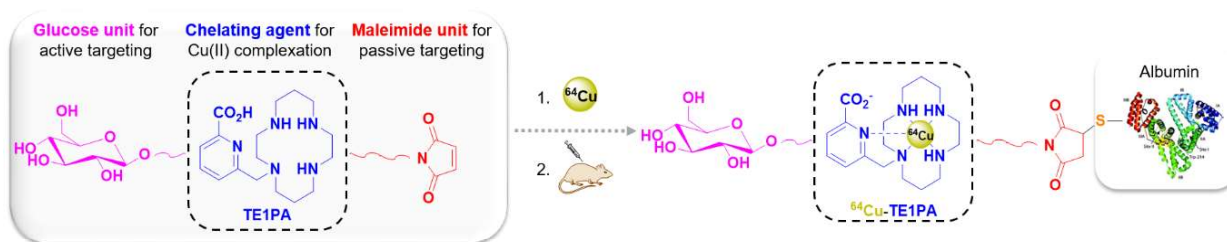


Figure 1 General structure of the TE1PA-based pro-conjugate (left) and radiopharmaceutical (right)

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Gold(III) cationic porphyrins to target G-quadruplex structures of HIV-1

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G-quadruplexes (G4s) are nucleic acid “knots” formed by guanine-rich sequences. These unusual structures are involved in key biological processes. They can be found in telomeres, oncogene promoters, RNAs, but also in viral genomes. For instance, HIV-1 genome contains 10 evolutionary conserved G4-forming sequences. Due to their unique structural features, very distinct from the known nucleic acids, G4s represent promising pharmacological targets for small molecules, namely G4-ligands. Indeed, gold(III) penta-cationic porphyrins, as specific G4 ligands, are able to inhibit HIV-1 infectivity and their antiviral activity correlated with their affinity for G4s [1]. Besides, porphyrin **1** was shown to prevent initiation of reverse transcription of HIV-1 in infected human cells [2]. This novel inhibition mechanism suggests that G4s play a crucial role in the very early steps of the HIV-1 replication cycle and that targeting viral G4s represents a promising antiviral avenue.

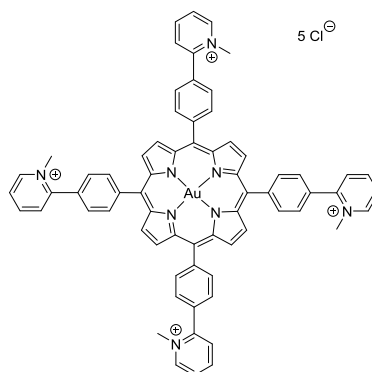


Fig 1. *meso*-5,10,15,20-tetrakis[4-(*N*-methyl-pyridinium-2-yl)phenyl]porphyrinato gold(III) pentachloride (**1**)

To better understand the molecular mechanism of action of the gold(III) porphyrins against HIV-1 replication we will present the design and preparation of a series of gold(III)-porphyrin and their affinity for G4 DNA.

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New Cobalt Complexes Bearing *P,N*-Ligands for Hydrosilylation of Ketones

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Cobalt catalysis has become more and more attractive,^[1] because of its earth abundance,^[2] low cost and relatively low toxicity. For example, cobalt complexes are known to be efficient catalysts in hydride transfer reactions.^[3] These reactions are involved in a wide range of organic transformations leading to various useful chemicals and synthetic building blocks. A very attractive reaction is hydrosilylation, allowing the simultaneous formation of C-H and Si-X (X=C, O, N,...) bonds under mild conditions and with an efficient atom economy.^[4] If cobalt-catalyzed hydrosilylation of alkenes and alkynes by complexes has been well investigated,^[5] that of ketones remains underdeveloped.^[6] Therefore, in this communication we wish to present the synthesis of unprecedented cobalt complexes bearing 8-phosphinoquinoline ligands, their characterization and their catalytic activity toward the hydrosilylation of ketones. Catalysis was efficient at low catalyst loading (1 mol%) under mild conditions. The efficiency differences depending on the ligand will be discussed.

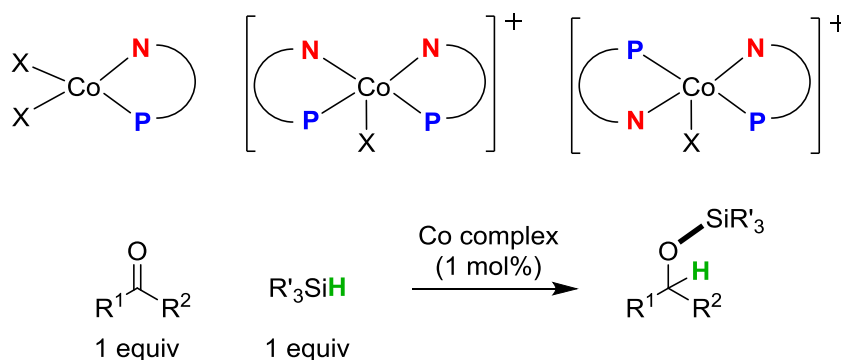


Figure 1 top: Cobalt^{II} complexes; bottom: Hydrosilylation reaction catalyzed by Co complex

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Controlling the interlocking of chiral self-assembled truxene-based cages

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The coordination-driven self-assembly strategy is remarkably efficient for building sophisticated discrete polygons and cages by association under thermodynamic control of polytopic ligands and complementary metal complexes.¹ Those systems inherently feature a cavity, prone to be used for host-guest purposes.²⁻⁵ Topologically more complex assemblies have appeared very recently in the literature: *interlocked cages*. Similarly, to the class of [2]-catenanes, interlocked cages are based on interpenetrated systems. While the first examples were essentially produced by serendipity as by-products along the metal-driven self-assembly process of discrete cages, the rationalization of their formation is subject to an intense attention.⁶⁻⁸ In this context, we have shown that a simple modification of a truxene-based ligand allows for controlling its self-assembly with a dinuclear complex toward a cage (Figure 1a)⁹ or two interlocked cages (Figure 1b)¹⁰.

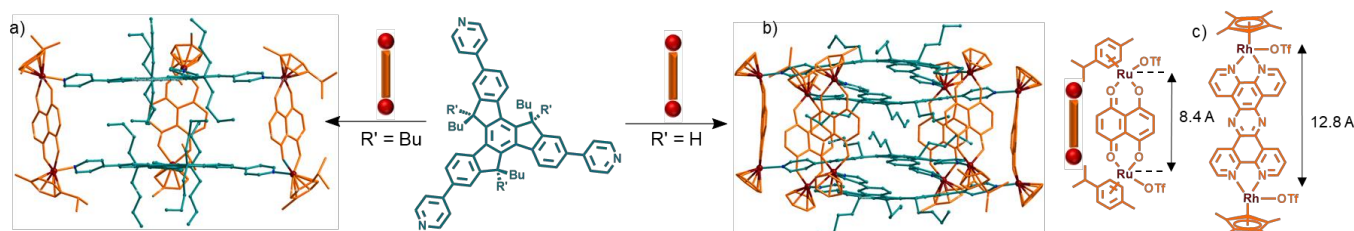


Figure 1. Reaction of truxene-based ligands (blue) with a bis-ruthenium complex (orange) affording a cage (a, X-Ray structure) or two interlocked cages (b, X-Ray structure); c) Extended bis-metallic complex.

These results will be discussed with a focus on *i)* the conditions that allows for controlling the cage interlocking and *ii)* the ability of this system to dissociate upon addition of a guest. Our last achievements with an extension of this approach to larger systems using an extended bis-metallic complex (Figure 1c) will also be presented.¹⁰

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10. Unpublished results, manuscript in preparation.

Functional hetero-poly-metallic complexes

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The design of functional molecular materials has attracted a great deal of attention in recent years. Owing to their molecular nature, they are associated with numerous advantages such as soft chemistry routes, light density, optical transparency or tuneable physical properties. Among these, our interest is focused upon hetero-poly-metallic complexes that have the potential of featuring luminescent, magnetic or photo-switching properties.

To obtain these hetero-poly-metallic complexes that combine up to four different metallic ions, we adopt a supramolecular approach that consists of using “polynuclear complexes as ligands”. In other words, polynuclear complexes are employed as precursors to obtain larger molecular architectures. This method is advantageous since it affords many variations in synthetic parameters, and the properties of the precursors are well established.

Our strategy of stepwise assembling the polynuclear precursors into supramolecular and dendritic assemblies essentially relies on cyanide- and oxalate-based coordination chemistry. The key building blocks are trinuclear complexes that feature High-Spin Molecule (HSM) and Single-Molecule Magnet (SMM) properties.

Employing dinuclear complexes and octacyanometalates as precursors, we have developed hetero-tri-metallic decanuclear squares and hetero-tetra-metallic species, that constitute a new class of SMMs.^[1,2] Here, we report the synthesis of several families of hetero-poly-metallic assemblies. The magnetic as well as the photophysical properties are also investigated.

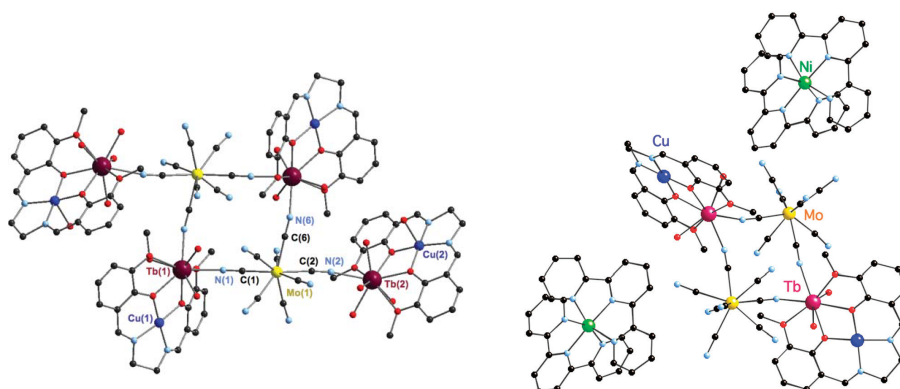


Figure 1 X-ray structure of the decanuclear square and the hetero-tetra-metallic assembly.

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Surface Engineering And Dispersion of Catalytically Active Gold In Porous Mesostructured Silica

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The fixation of catalytic metal complexes is a very active field in heterogeneous catalysis as it combines selectivity of homogeneous catalysis with higher robustness, easier separation and possibility of recycling. The growing interest for the very specific catalytic activity of gold in cyclization and oxidation reactions involving Au (III) and Au(I) ions prompted us to investigate this metal. However, the interfacial chemistry of ionic gold is not yet developed as it readily reduces to Au (0) atoms that migrates and aggregates irreversibly. The idea is to stabilize single Au (III) ions on a surface to avoid the formation of Au(I) pairs during the catalytic cycles. These pairs of ions indeed dismutate into Au (III) and Au (0) pairs opening the irreversible route of metallic gold at room temperature.

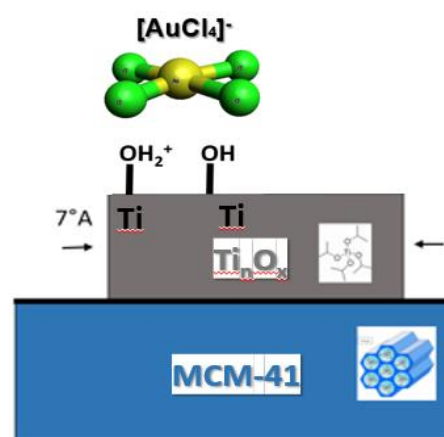


Figure 1: Heterogeneous catalyst

We propose to investigate stabilization of single Au (III) ions in mesoporous silica based materials having a particularly large surface areas (1000 g/nm²) and appropriate pores (> 3 nm) for efficient molecular internal diffusion and useful catalytic application. The stabilization is obtained by selective adsorption on Ti_nO_x oxohydroxotitanium subnano islands,¹ n = 3, size ~ 0.7 nm – themselves fixed on the siliceous internal pores of the mesoporous silica support by grafting titanium alkoxides in the presence of a molecular pattern.

Then AuCl₄⁻ ions are selectively adsorbed from a water solution by TiOH₂⁺ groups in the pH range 2 to 6, between the ZPC SiO₂ and TiO₂. Washing with water confirms that without Ti_nO_x islands gold retention drops from 90 to 0.5%.

To further investigate the elimination of chloride around supported gold, we revisited the successive equilibria of AuCl₄⁻ with [AuCl_x(OH)_y]⁻ (x+y = 4) in solution for future quantitative analysis of the UV-visible spectra. We were surprised by some contradictions concerning the intermediate [AuCl₃(OH)]⁻, [AuCl₂(OH)₂]⁻ and [AuCl(OH)₃]⁻ species comparing reported UV and Raman spectroscopic studies. This prompted us to investigate the UV range 250 to 400 nm not yet reported.² We discovered new bands, 3 isosbestic points and a more precise value of the molar extinction coefficient for [AuCl₄]⁻.

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² I. V. Mironova, V. Yu. Kharlamovaa, *Russian Journal of Inorganic Chemistry*, **2020**, *65*, 391.

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Rational design of metal nanoparticles: ligand effects, addition of a second metal, and application in catalysis

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Chemistry can contribute to the sustainable society with solutions for environmental issues providing efficient chemical processes and catalysis. Increasingly complex processes and systems need designing highly effective advanced catalytic systems. In the past, homogeneous and heterogeneous catalysis were learned and studied as distinct disciplines. Different synthetic approaches, different characterization techniques, and so on. In the past years, these differences have dissolved to give a plethora of intermediary concepts; colloidal nanoparticles decorated with ligands typically devoted to modulate metallic centers for homogeneous catalysts, atomically defined metallic species in supports, are examples of the precision in the design of efficient catalyst that are reached nowadays. Our contribution in this field tries to do a transition towards earth-abundant, cheap, non-toxic and renewable materials for catalysis, for now producing bimetallic Ni and Cu based catalysts. We have gathered now some knowledge about the interaction of ligands towards the metallic nanoparticle surface, and the effect on catalysis, using a combination of experimental and theoretical tools, which we would like to extrapolate to earth-

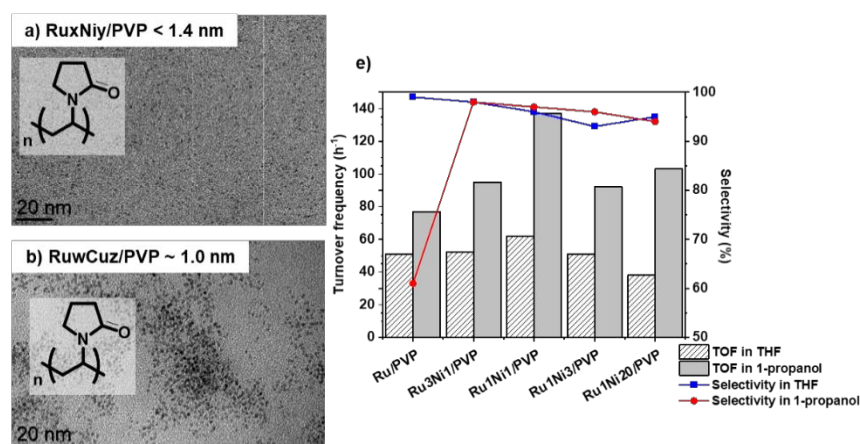


Figure 1 a) ultrasmall RuNi/PVP and b) RuCu/PVP nanoparticles; and e) TOF and selectivity in the selective hydrogenation of furfural

abundant metallic surfaces. Here we would like to present our last results in the synthesis of RuNi and RuCu bimetallic catalysts to upgrade biomass derivatives, how ligands interact with RuNi bimetallic surfaces, doing the link with the results we obtained in the past using Ru-based catalysts.

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A Bis-Acrinium Macrocycle as Multi-Responsive Receptor and Selective Phase-Transfer Agent of Perylene

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Supramolecular receptors are systems having recognition properties that lead to the formation of supramolecular complexes in the presence of guest molecules. The recognition properties are defined by the nature of the cavity, shape, size, and electronics properties of the receptors. The acridinium core is a building block with a great potential in supramolecular chemistry. Indeed, it is an electron-deficient polyaromatic unit (presence of a positive charge) and it can interact with electron rich polyaromatic guests through π -donor/ π -acceptor interactions.¹⁻² In addition, acridinium units have chemiochromic, electrochromic and photochromic properties making them multi-responses units.³⁻⁴⁻⁵

A bis-acridinium cyclophane incorporating switchable acridinium moieties incorporating a 3,5-dipyridylanisole spacer was successfully synthesized (**Figure 1**).⁶ Once obtained, it was studied as a multi-responsive host for polycyclic aromatic hydrocarbon guests. Complexation of perylene was shown to be the most effective among anthracene and naphthalene. Interestingly, effective catch and release of the guest was triggered by both chemical (proton/hydroxide) and redox stimuli. Moreover, the dicationic host was also easily switched between organic and perfluorocarbon phases for applications related to the enrichment of perylene from a mixture of polycyclic aromatic hydrocarbons.

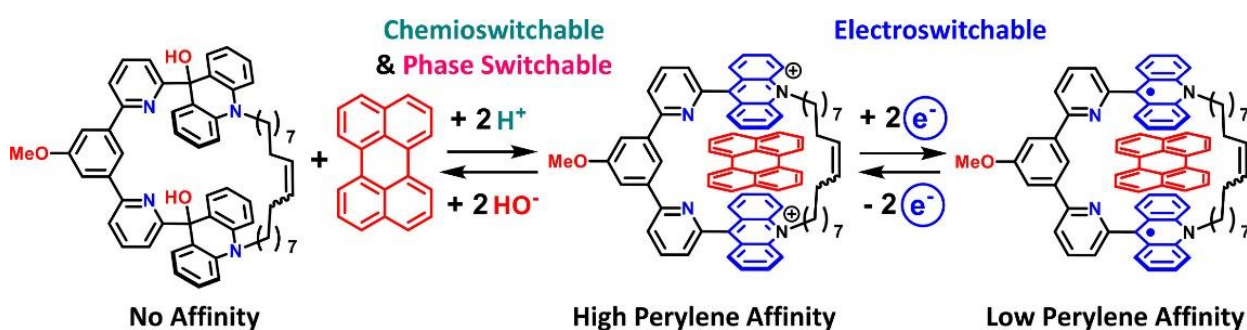


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Synthesis, characterizations and first biological evaluations of potential corono and clipcarbenes: new *bis*-imidazolium-*bis*-heterocycle macrocyclic ligands

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In recent years, a considerable number of N-Heterocyclic Carbenes (NHCs) and their metal complexes have garnered extensive research attention with a broadening of their applications [1][2][3][4][5]. However, only few studies focus on the preparation of structures combining both a “macrocycle” and an “imidazolium” and of their metal coordination complexes.

We describe two successful synthesis ways of a new macrocyclic imidazolium salt family with an original structure covalently bearing two imidazoliums moieties – as NHC precursors and two *bis*-heterocyclic units (bipyridine or bithiazole). We also report the synthesis of new flexible compounds, *N*-*bis*-imidazole-*bis*-heterocycles and *N*-*bis*-imidazolium-*bis*-heterocyclic ligands, obtained through the preparation of the above-mentioned macrocycles. NMR and mass spectroscopy characterizations of each new compound are realized. The molecular structures of two of the macrocyclic salts, the *N*-*bis*-imidazolium-*bis*-bipyridine and the *N*-*bis*-imidazolium-*bis*-bithiazole obtained by single –crystal X-ray diffractions are described. In parallel, biological evaluations of the macrocycles L1 to L3 are conducted. The first results obtained from the cytotoxicity and anti-bacterial studies are given.

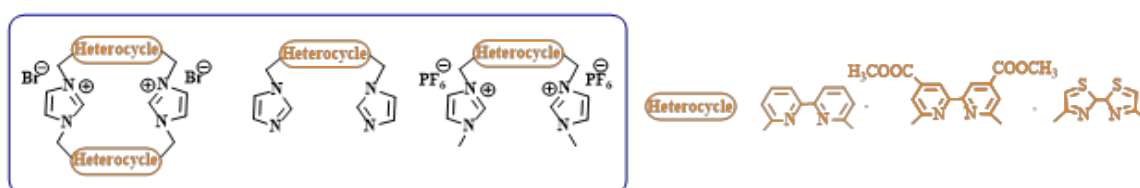


Figure 1 : Scheme of the new macrocyclic imidazolium salt family and the new flexible compounds

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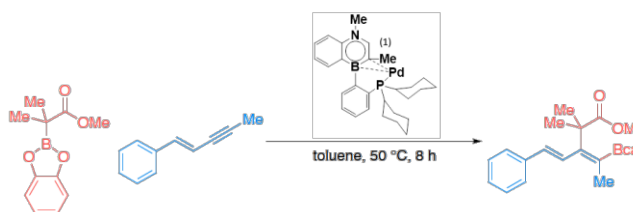
Palladium Catalyzed Carboboration of Internal 1,3-Enynes with Carbon-Bound Boron Enolates: mechanistic studies by computational approach.

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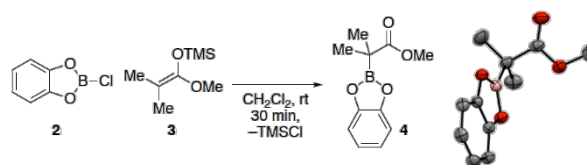
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In addition to their utility as reactive substrates in Suzuki-Miyaura cross coupling reaction, alkenyl boronates have received a great deal of attention as versatile building blocks in organic synthesis¹ due to their efficient conversion into various functional groups. Nevertheless, unlike the di²- and trisubstituted³ alkenyl boronates, the synthesis of tetrasubstituted⁴ alkenyl boronates often face regio- and dia-stereoselectivity issues for internal alkynes. Recently, Liu *et al.* have shown that 1,4-azaborine-Senphos Palladium complex (**1**) catalyzed carboboration of 1,3 enynes with a new discovered C-boron enolates family as the reagent to produce tetra-substituted alkenes in high regio- and stereoselectivity. In order to have a better insight on this reaction, DFT calculations were performed jointly with the experimental approach. We first shed light on the formation of C-catecholboron enolate **4** from reaction between silylketene acetal **3** and catecholborane **2**. Then, computational mechanistic investigations have been carried out to describe in detail the privileged pathway involved in this carboboration reaction. Three mechanisms have been considered i) classical oxidative addition mechanism in which Pd metal center can directly activate the C-B bond or ii) outer sphere oxidative addition mechanism; iii) cooperative oxidative addition mechanism, going through a stabilized Pd- π -complex resulting from the interaction between enyne and catalyst. In this communication, we will describe theoretically the different pathways and discuss in detail the privileged one.



Scheme 1. Regio- and Stereoselective Synthesis of Tetrasubstituted Alkenyl boronates



Scheme 2. Formation of C-Boron Enolates without Boron Quaternization

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New Zinc Chelating Agents for Therapeutic Purposes

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In addition to its structural and catalytic role in human organism, zinc(II) is well known as key regulator of apoptosis. Many groups reported the ability of various linear chelators possessing high affinity for zinc(II), to decrease intracellular zinc(II) level and induce apoptotic cell death in cancer cells^{1,2}.

In our research group, macrocyclic chelators platform have already been described as good zinc(II) chelators³. This work aims to explore the relation between the chemical structure and biological activity of three chelators which differentiate by the number of coordinating arms (**Figure 1A**). This presentation will focus on the synthesis of the chelators and the study of the thermodynamic properties of the zinc(II) complexes. Then, the first biological results obtained by real-time mortality analysis of the chelators in various cells lines using Incucyte technology will be discussed (**Figure 1B**).

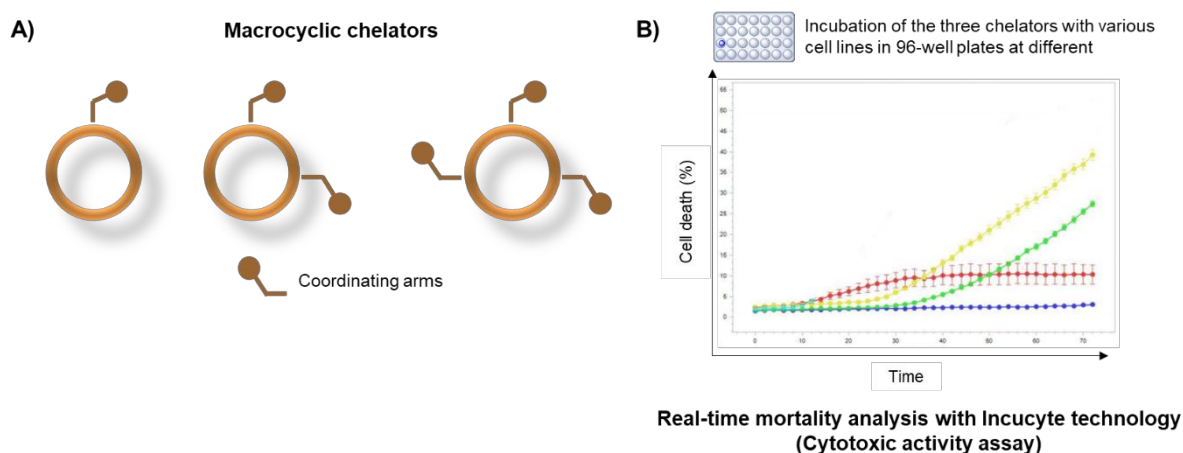


Figure 1 Structure-activity relationship of macrocyclic zinc(II) chelators

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Reactive bis(iminophosphoranyl)phosphide ligands afford new Ti-Ir and Ti-Rh heterobimetallic complexes

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Bis(iminophosphoranyl)methanediide ligands (BIPM) are exceptionally versatile species to coordinate a wide range of metals across the periodic table.¹⁻³ Due to the strength of C-P bonds, BIPM are quite robust and essentially act as ancillary ligands. Our group has recently reported on the use of valence isoelectronic bis(iminophosphoranyl)phosphide ligands (BIPP) to stabilize group IV metals.⁴ In this contribution, we show that BIPP undergo facile P-P bond cleavage at titanium in the presence of alkynes (Figure 1).

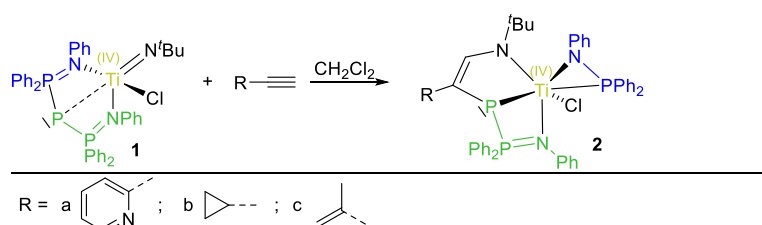


Figure 1: Rearrangement complex formation

Reaction of **2b** with $\frac{1}{2}$ [M(cod)Cl]₂ leads to the heterobimetallic complexes **4** where all phosphorus atoms are coordinated to the late transition metal (Figure 2). Reactivity of complex **4a** was investigated and showed activation potential towards the C=O bond of ferrocenecarboxaldehyde to give **5** (Figures 3 and 4).

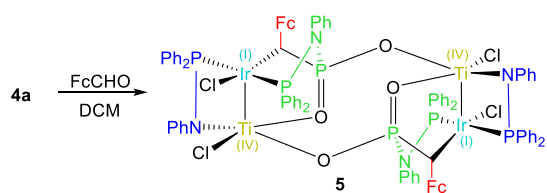


Figure 3: C=O cleavage by **4a**

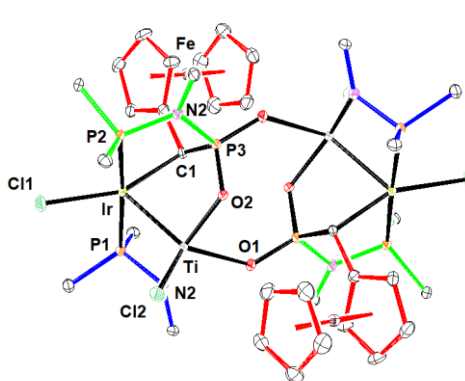
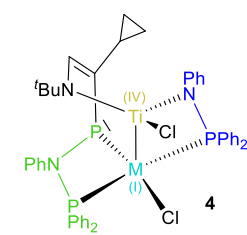


Figure 4: XRD structure of **5**



M = a : Ir ; b : Rh

Figure 2: Bimetallic complexes

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Graphene Oxide as a Structural Directing Agent of MOFs

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Due to their huge surface areas, topological diversity, and functional tunability, MOFs have sparked a high interest for different applications including gas storage/separation, catalysis, sensing or biomedicine¹. However, these porous hybrid materials are mostly obtained in the form of a polycrystalline powder or spherical nanospheres. One of the main challenges for their practical application is to control the crystal size, morphology and multiscale porosity of these materials while developing adequate shaping methods. For that purpose, one of the strategies reported in literature consists to combine MOFs with different carbon-based materials (polymers, graphene, carbon nanotubes, ...) ². A recent work investigated the use of GO nanoscrolls as structure directing agents to form single crystal aluminum-based MOF nanowires (NWs)³. Following this approach, it was possible to obtain hierarchical porous MOF/GO composites with a specific microstructure that allowed a homogeneous dispersion of MOF NWs in the GO matrix, without any agglomeration of MOF NPs or restacked GO layers (Figure 1). Hence, throughout this PhD project, we aim to extend this concept to aluminum-based MOFs with high permanent porosity. In this communication, we will present the synthesis optimization of these MOFs/GO composites as well as their structural and physico-chemical properties.

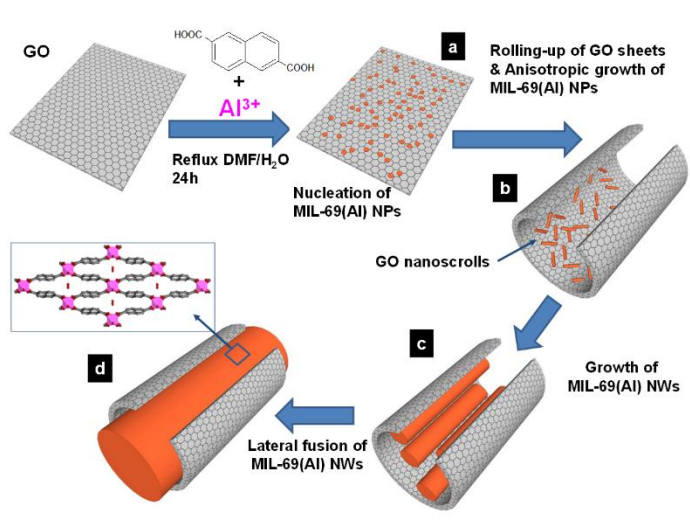


Figure 1 Schematic mechanism of the formation of MIL-69(Al) NWs³

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Enamidyl Vinyl Ketones to generate Molecular Complexity

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Despite the exhaustive literature on enamines and enamides, tertiary enamides have only recently proved their enamidic reactivity toward several classes of electrophiles.¹ Thus, we have shown that ynamides incorporating an *N*-imide can be transformed into tertiary enamides equipped with a precursor of an *N*-acyliminium ion (NAI). In acidic medium, the tertiary enamide adds to the *N*-acyliminium species to form diazepine drug substructures.²

In this context, we focused on enamidyl vinyl ketones to trigger Nazarov reactions to access complex polycyclic diazepine motifs. Following the concept of atom economy, we have shown that cyclopentenoid-fused diazepines could be obtained diastereoselectively using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in one pot through a domino *N*-acyliminium ion trapping/Nazarov reaction, simultaneously generating three new stereogenic centers.³ The particular structural design of the cross-conjugated dienone dictates the torquoselectivity observed in this polarized Nazarov reaction. Various *N*-bridgehead polycyclic scaffolds of putative pharmacological interest were obtained.

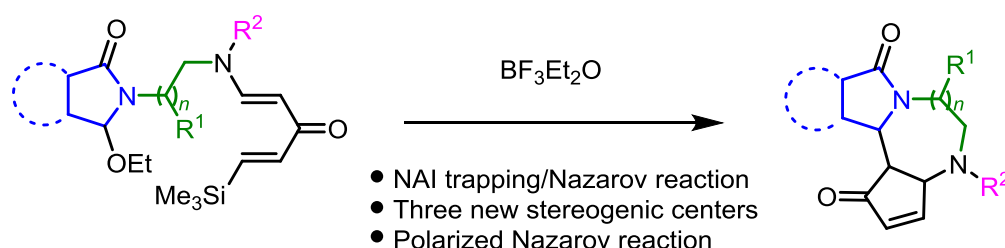


Figure 1 Domino reaction : *N*-Acyliminium Ion trapping and Nazarov cyclization

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