Coordination Chemistry of Copper in Biology and Medicine

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Abstract

Copper ions are essential for almost all living beings and mainly occur in the two redox states Cu(I) and Cu(II). Cu(I/II) are almost exclusively coordinated to binding sites in proteins with high affinity enabling a tight control of its chemistry. Cu ions bound outside the physiological binding sites are potentially dangerous, often *via* its high capacity to activate O_2 to form reactive oxygen species. Several diseases have been linked to a dyshomeostasis of copper such as Wilson's and Menkes genetic disorders, Alzheimer's disease, cancer etc... Thus, interfering in copper metabolism *via* small ligands is a widely investigated therapeutic approach and, in some cases like Wilson disease, routinely used in clinics.

During the last years we worked on the Cu chemistry of several biological relevant peptides, chelators and complexes. This includes the amyloid-β peptide related to Alzheimer's disease (*1 for recent review*), several classical ligand types (e.g. thiosemicarbazones) studied for their anticancer or antimicrobial applications (*2*) and the development of a selective Cu(II)-sensor for biological applications (*3*).

In all this cases, the design of a Cu-ligand to control the Cu-coordination chemistry in a biological environment is extremely challenging (*2,4*). Main issues are the interdependent parameters of stability constants, redox potential/reactivity, selectivity against other essential metal ions, the very different coordination chemistry between Cu(I) and (II), and metal exchange rates with biomolecules. Recent insights from our group in this area will be discussed.

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THE EFFECT OF BRIDGE SUBSTITUTION IN NHC-PHOSPHINE Mn(I) COMPLEXES ON COOPERATIVE H_2 ACTIVATION AND CATALYSIS

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Keywords : Manganese complexes ; *N*-heterocyclic carbenes ; Phosphonium ylides ; Hydrogenation.

Nowadays the design of well-defined Mn(I) catalysts for (de)hydrogenation-type processes[1] became one of the most popular directions in homogeneous catalysis. Despite the Mn-based catalytic systems with pincer-type ligands still remain the most studied, some octahedral complexes *fac*-[(L–L')$Mn(CO)_3Br$] bearing less structurally elaborated bidentate ligands could be competitive in terms of catalytic activity and/or substrate scope.[2] In particular, we have recently shown that the association of phosphine and NHC donors in Mn(I) complex *fac*-[$(Ph_2PCH_2NHC)Mn(CO)_3Br$] (**1a**, Figure 1, up) resulted in the development of catalytic system for ketone hydrogenation being one of the most active in Mn series.[3] The mechanistic investigation of pre-catalyst activation step (Fig. 1, down) revealed the initial formation of cyclometallated form **2a** upon deprotonation, its isomerization to the non-classical ylide intermediate **3a** and cooperative H_2 activation to form the corresponding hydride product **4a**. Inspired by our recent observation of easier H_2 activation for the related Mn(I) dppm complexes *fac*-[$(Ph_2PCH(R)PPh_2)Mn(CO)_3Br$] upon the ligand bridge substitution with phenyl group,[4] we report herein that such modification of NHC-phosphine complex **1a** significantly improved catalytic activity. Experimental and DFT studies of both stoichiometric H_2 activation and catalytic cycle for acetophenone hydrogenation rationalizing the beneficial effect of the phenyl group will be also presented.

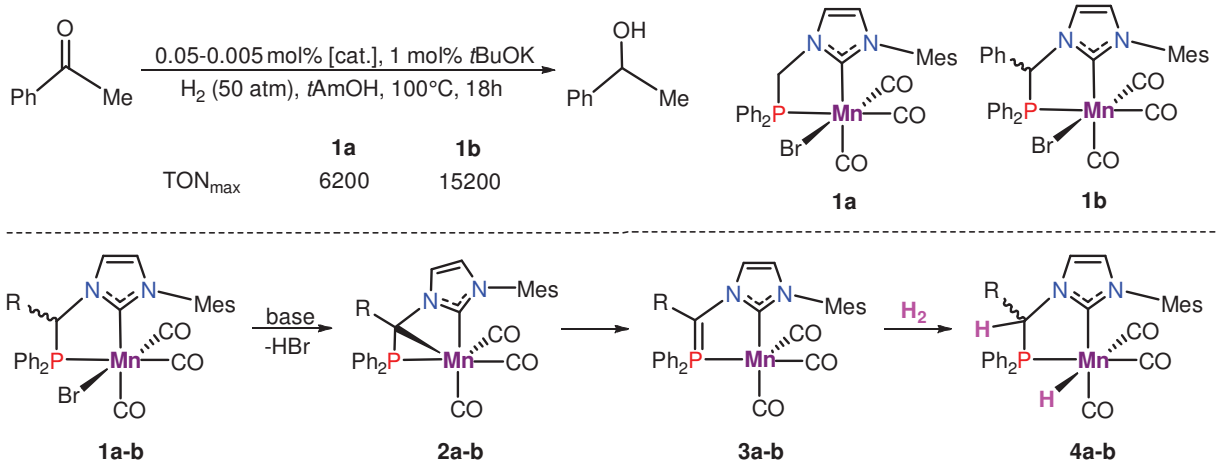

Fig. 1 Cooperative dihydrogen activation by Mn(I) complexes bearing phosphine-NHC ligands and their application in catalytic hydrogenation of acetophenone.

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Acknowledgments
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Assemblage polymétallique luminescent d'ions Cu(I) : relation conformères/propriétés et sensibilité aux stimuli externes.

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Keywords : Cu(I), assemblage polymétallique, luminescence, conformères

Face à la demande croissante de matériaux photo-fonctionnels de plus en plus performants pour des applications telles que les OLEDs ou les capteurs, les composés moléculaires à base d'ions Cu(I) s'avèrent être une alternative intéressante aux matériaux plus coûteux.[1–3] Ils montrent des propriétés de luminescence particulièrement attrayantes grâce aux différents processus d'émission radiative permis, tels que la fluorescence retardée thermiquement activée (TADF).
Afin de s'affranchir de la grande labilité de l'ion Cu(I), nous avons développé une voie de synthèse à partir de briques moléculaires polymétalliques pré-organisées.[4,5] En limitant la flexibilité conformationnelle et directionelle des liaisons de ces complexes, nous sommes parvenus à préparer directement et sélectivement des édifices supramoléculaires complexes aux structures et propriétés photophysiques originales. Ainsi, un métallacycle polymétallique, noté $Cu^{I}_{8}Pd^{II}_{1}$, a été obtenu.[4,5]

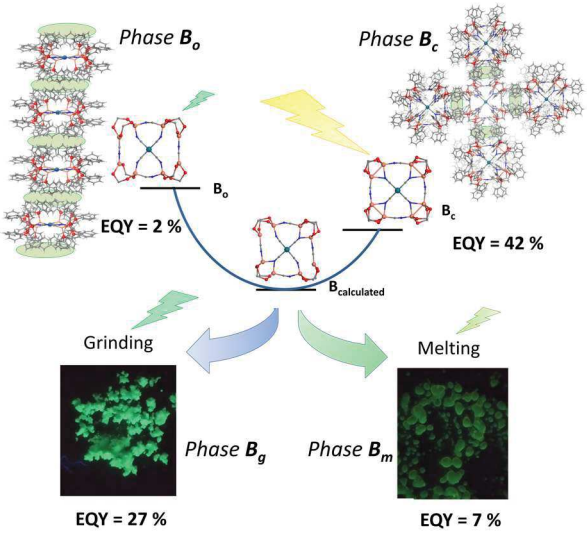

Fig. 1 : Empilements cristallins, structures des différents conformères et photos sous irraditation UV (EQY = emission quantum yield)

Deux conformères peuvent être isolés à l'état solide, présentants des modes de coordination des ligands cyano internes différents (μ^2-*forme ouverte* $\boldsymbol{B_o}$ ou μ^3-*forme fermée* $\boldsymbol{B_c}$, Fig.1) et des distances intermétalliques Cu^{I}-Cu^{I} distinctes.
Chaque conformère possède un empilement cristallin et des propriétés de luminescence qui lui sont propres (Fig. 1). Les interactions non-covalentes entre les métallacycles s'avèrent être cruciales pour expliquer les relations structure/propriété observées.

Des propriétés d'émission à l'état solide, affectées par des stimuli externes, ont pu être anticipées pour ce composé $Cu^{I}_{8}Pd^{II}_{1}$, sur la base des modifications de l'arrangement moléculaire par broyage *($\boldsymbol{B_g}$)* ou par fusion *($\boldsymbol{B_m}$)*. Nous présenterons l'étude expérimentale et théorique détaillée des phases obtenues, qui nous a permis de rationaliser les comportements observés.

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Hofmeister effect in the Keggin-type polyoxometalate series

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Keywords: host-guest association; polyoxometalate; chaotropic effect

Texte: Polyoxometalates (POMs) represent a class of water-soluble metal-oxo clusters built from group V and VI transition metals in their highest oxidation states, e.g., V^{V}, Mo^{VI}, and W^{VI}. This class of compounds exhibits a wide range of structures and chemical compositions, offering a wide variety of properties that lead to applications in catalysis, medicine and materials science.[1] POMs are able to form strong interactions with neutral surfaces or non-ionic molecules such as organic macrocycles.[2] The archetypal Keggin-type heteropolyanions $[XW_{12}O_{40}]^{n-}$ have the ability to form stepwise inclusion complexes with the toroidal γ-cyclodextrin (γ-CD) in aqueous solution.[3]

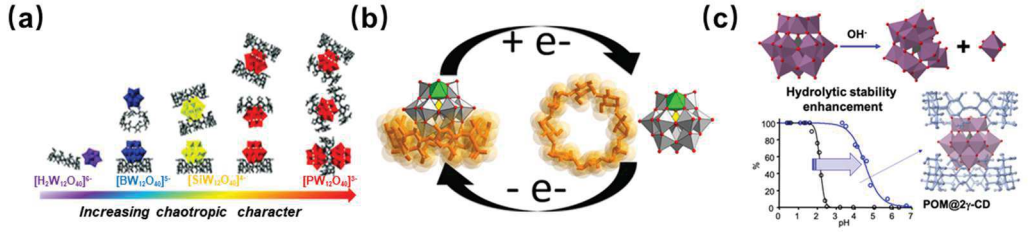

Fig.1. (a) Illustration of the most representative binding modes involved in the supramolecular assemblies built from γ-CD and Keggin ions. (b) Structure schematic diagram of the redox responsive POM@γ-CD complex. (c) Effect of medium on stability domains of γ-CD and $[PW_{12}O_{40}]^{3-}$,

In this presentation, we will first demonstrate that this intriguing host-guest association between POMs and CDs is driven by the chaotropic effect [4] (see Figure 1a) which consists of solvent effect based on water structure recovery process resulting from the desolvation of the interacting units, i.e., POM and cavitand. As a consequence, the binding constant between γ-CD and $[XW_{12}O_{40}]^{n-}$ anions can be controlled by the global charge density of the POM from n- = 3- to 6-. This can be achieved by changing the heteroelement X, where X = P, Si, B, or H_2, but also by changing the redox state of the POM. Indeed, by using a series of molybdenum and vanadium monosubstituted anions, controlled reduced species could be performed delivering unique redox-responsive host guest systems (see Figure 1b).[5] At last but not least, we will show that the encapsulation of the POM within the CD provides an increase of the hydrolytic stability of inorganic guest, herein the Keggin-type polyoxometalate $[PM_{12}O_{40}]^{3-}$ anion (M = W^{VI} or Mo^{VI}).[6] As shown in Figure 1c, a shift of up to 2-3 higher pH units is observed for stability domain of $[PW_{12}O_{40}]^{3-}$ species.

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Phase change luminescent gold-thiolate coordination polymers

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Keywords: coordination polymer, gold-thiolate, phase change, photoemission.

To meet the exponentially growing demand for data recording, various information storage technologies are being developed. Phase Change Random Access Memory (PCRAM) is known to be very promising to establish itself as the next generation of non-volatile memory due to its excellent operating speeds and endurance. The principle of these PCRAM, is based on the reversible transition with the temperature of a material between its amorphous and crystalline phases that allows writing and erasure; reading exploiting the contrast of resistivity between these two phases. The materials used for this type of storage are chalcogenides, however, these inorganic systems still have limitations, including high transition temperatures, around 600°C, and limited miniaturization due to their intrinsic friability.[1] In this presentation, we will use Phase Change Coordination Polymers (PCCPs) as an alternative to chalcogenides. The PCCPs we are using are gold-thiolate, $[Au(SR)]_n$, made of thiolate ligands and d^{10} Au(I) to have highly stable and photoluminescent solids.[2] We will discuss the synthesis of new compounds: $[Au(p\text{-}SPhX)]_n$ (X = F, Cl, Br) and the effect of the halogen atoms on the formation of 1D or 2D structures and the resulting photophysical properties of the CPs. Then, we will focus on $[Au(p\text{-}SPhF)]_n$ which shows a great ability for cyclic amorphous-to-crystalline phase change associated with a ON-OFF switch of the emission (**Fig.1**).

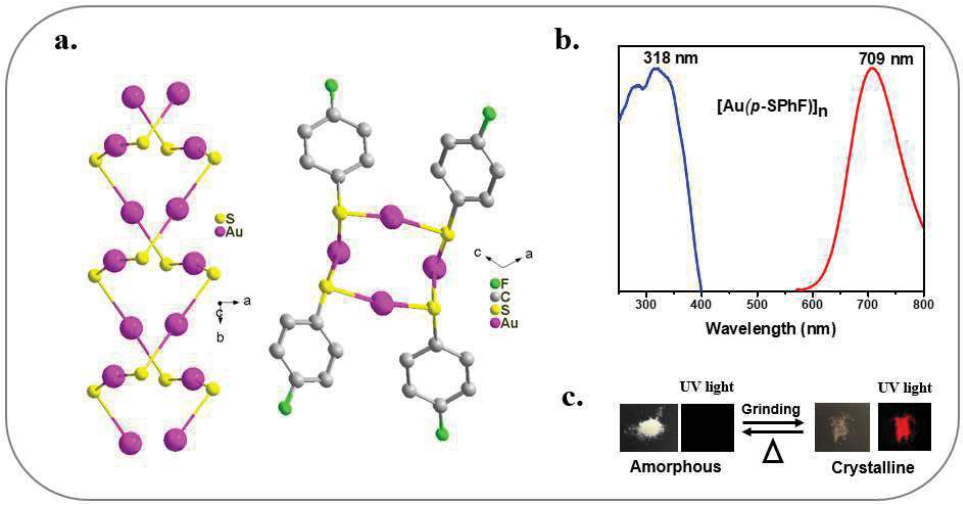

Fig. 1. The phase change in $[Au(p\text{-}SPhF)]_n$ CP. ***a.****, its 1D structure,* ***b.****, the excitation/emission spectra at room temperature and* ***c.****, photos of its reversible amorphous to crystalline phase under heat and grinding.*

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Assemblage MOF_CD : vers des matériaux hybrides originaux ?

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Keywords : MOF, cyclodextrines, greffage, assemblage MOF_CD, UiO-66-R

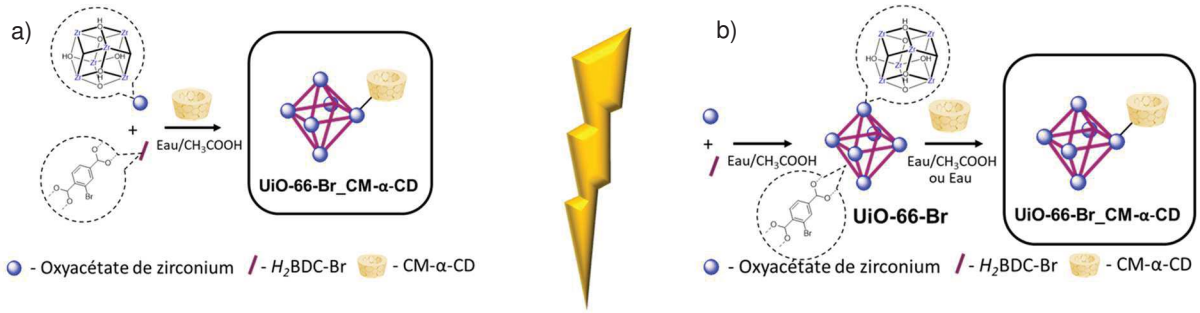
Texte:

Les réseaux métallo-organiques plus habituellement appelés “Metal Organic Frameworks” (MOF) sont des matériaux poreux synthétiques hybrides. Ils possèdent une grande malléabilité structurale, ce qui permet de modifier la taille et la nature de leurs pores en fonction de l’application désirée. Ces matériaux à porosité organisée sont composés d’ions ou clusters métalliques reliés entre eux par un motif organique.

Les cyclodextrines (CDs) sont des oligosaccharides cycliques constitués de sous-unités glucopyranoses pontées en α (1-4). Ces molécules ont la forme d’un cône tronqué formant une cavité hydrophobe en leur centre et ont une surface hydrophile. Nous avons déjà montré qu’il était possible d’utiliser l’α-CD et la β-CD en tant que co-modulateur de synthèse de MOF UiO-66-R en milieu aqueux acide. Cela nous a permis d’améliorer les propriétés texturales de ces MOFs et notamment des UiO-66-NH_2 et UiO-66-Br grâce à une régulation de la croissance des cristaux de MOFs et une meilleure dispersion des réactifs dans cette méthode « one pot » qui ne voit en aucun cas les cyclodextrines se fixer sur le matériau final. [1,2]

Suite à ces travaux, nous avons cherché à concevoir des matériaux hybrides originaux alliant le MOF UiO-66-Br et une cyclodextrine modifiée. Nous avons choisi d’utiliser une cyclodextrine carboxyméthylée (CM-α-CD) afin de profiter des fonctions acides carboxyliques qu’elle porte pour les greffer par liaison de coordination sur le MOF. Nous proposons ici une méthode de synthèse dite « one pot » identique à celle des travaux précédents dans laquelle seule la CD utilisée diffère. Il est à noter que la formation de matériaux hybrides MOF_CD par une méthode « one pot » n’a jamais été décrite dans la littérature. A titre de contrôle, une voie de synthèse de ces matériaux hybrides par modification post-synthétique (classiquement retrouvée dans la littérature) a également été étudiée et une comparaison des deux méthodes a été effectuée.

Fig. 1 Schéma réactionnel de la synthèse de MOF hybride UiO-66-Br_CM-α-CD : a) voie de synthèse en une seule étape ; b) voie de synthèse par modification post-synthétique



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BRIGHT RED-EMITTING HETERO-BIMETALLIC COMPLEXES FOR EFFICIENT LIGHT-EMITTING ELECTROCHEMICAL CELLS

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Keywords: cyclometalating ligands; phosphorescent complexes; N-heterocyclic carbenes; iridium emitters; heterometallic complexes; light-emitting electrochemical cells

Summary: Phosphorescent complexes have been extensively investigated in the last few decades in the fields of organometallic chemistry as well as materials science due to their outstanding photophysical and redox properties.[1] Following the seminal work of Thompson and Forrest,[2] great interest in these classes of photoactive compounds has emerged mainly driven by their application as triplet emitters in phosphorescent light-emitting devices, such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs).[1] Nevertheless, achieving bright emission in the red and near infrared (NIR) region is highly challenging due to *energy gap law* consideration. Hence, efficient red/NIR light-emitting devices are still scarce, inspite of their importance in fields such as biomedical and display technology.

Herein, our most recent results in the field will be presented including a novel class of phosphorescent cationic heterobimetallic Ir^{III}/M^{I} complexes, where M^{I} = Cu^{I} and Au^{I} where the two metal centers are connected by the hybrid bridging 1,3-dimesityl-5-acetylimidazol-2-ylidene-4-olate (IMesAcac)[3] ligand that combines both a chelating acetylacetonato-like and a monodentate N-heterocyclic carbene site coordinated onto an Ir^{III} and a M^{I} center, respectively. These cationic bimetallic species display vibrant red emission with up to two-fold increase of the photoluminescence quantum yield and radiative rate constant compared to the corresponding mononuclear benchmarks,[4] and achieve record PLQY up to 77%. This finding is associated to the smaller energy gap between the metal-to-ligand charge transfer (^{1,3}MLCT) and the ligand center (^{3}LC) manifolds that mix via spin-orbit coupling and configurational interaction. Finally, their successful application as electroluminescent materials in light-emitting electrochemical cells (LECs) will be presented, which show external quantum efficiency up to 6%. In spite of the simple single-layer solution-processed device architecture, these values are the highest one for bimetallic emitters to date and amongst the highest for red LECs.[5]

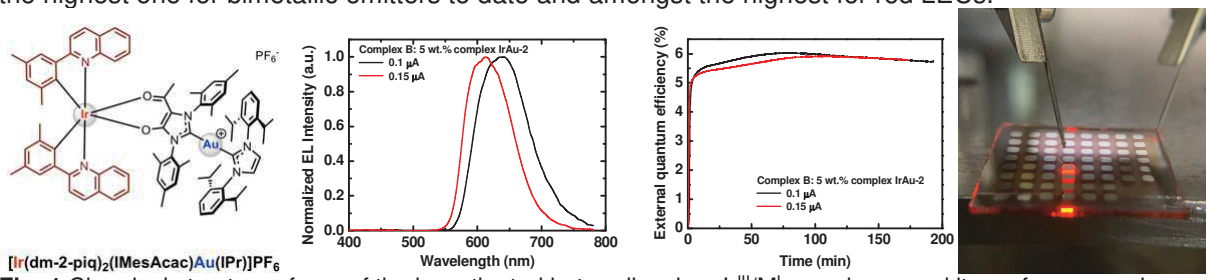

Fig. 1 Chemical structure of one of the investigated heterodinuclear Ir^{III}/M^{I} complexes and its performances in LEC devices.

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Proton-coupled multi-electron transfer in polyoxometalates containing three vanadium centers

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The chemistry of polyoxometalates containing V centres knows a renewing of interest due to their appealing redox properties that offer potential applications in energy storage[1,2] (Li-ion batteries, redox flow-batteries) as well as in catalysis[3] (activation of O_2). In this context, our research aims to explore the synthesis, the solution behaviour and the redox properties of V-based POMs.

In this communication, we will present first the synthesis and structural characterizations (X-ray structure and multinuclear ^{17}O, ^{51}V, ^{183}W NMR) of a series of POMs containing three V centres that have been obtained from condensation of vanadates with tri-lacunary Keggin type-POMs {AsW_9} in aqueous solution. The resulting compounds exhibit either a Keggin-type or a sandwich like arrangements. In these structures, the vanadium polyhedra can be: i) isolated from each other (compound $[(AsW_9O_{33})_2(VO)_3]^{9/12-}$), connected together by corners (compound $[AsW_9V_3O_{40}]^{6/9-}$) or by edges (compound $[AsW_9V_3O_{39}]^{6/9-}$). In a second part, we will show the investigations of electrochemical properties of these POMs that highlights that the redox potentials of the V centres can be tuned in large extend by their location within the metal-oxo frameworks. Importantly, the redox properties appear strongly altered in the 0.5 – 5 pH range, consistent with proton-coupled electron transfers (PCET).

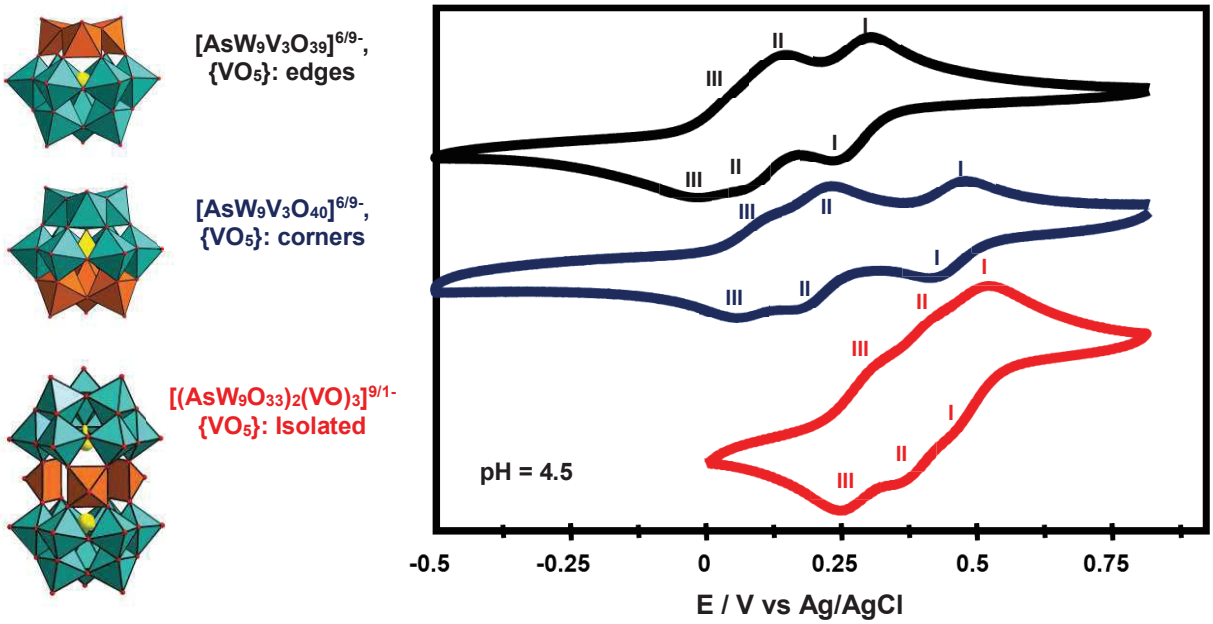

Figure. (Left) Polyhedral representations of the tri-vanadium containing POMs built from {AsW9} units. (Right) Electrochemical signatures of these POMs in aqueous solution (pH=4.5).

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Binary supercrystal assembly combining chemical and mathematical approaches

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Keywords: Self-assembly, Nanoparticle, Ligand effect, Superlattice, Amine, Thiol

Organization of nano-objects of different natures leads to superstructures[1] combining their functional properties[2] (magnetic, semiconducting, luminescent, catalytic, etc.). A broad range of structuration may be envisioned, depending on the processes of self-assembly of the building blocks: periodic superlattices, quasicrystals and aperiodic assemblies. The presentation will be focused on the formation of periodic assemblies of spherical nanoparticles, and will detail some effects of the ligands on the formation of superlattices. Work on periodic single component system, as well as on binary assemblies will be presented.

Among the parameters that affect nanoparticle self-assembly, the stabilising coordination sphere of ligands plays a main role. Several works have been reported revealing the importance of the size ratio between the ligand length and the radius of the nanocrystal core[3]. In a first part, we will explain how the presence of an excess of ligand in the system can also have a strong influence of the assembly. Working with small gold nanoparticles in presence of oleylamine (OAm), we have observed that an increasing excess of ligands leads to a structural change of the superlattice structure from FCC to BCC (Fig. 1). Interestingly, a novel primitive hexagonal structure has been observed for some nanoparticle sizes. In a second part, ligand size effects will be detailed in the frame of binary assembly of gold and ruthenium nanoparticles.

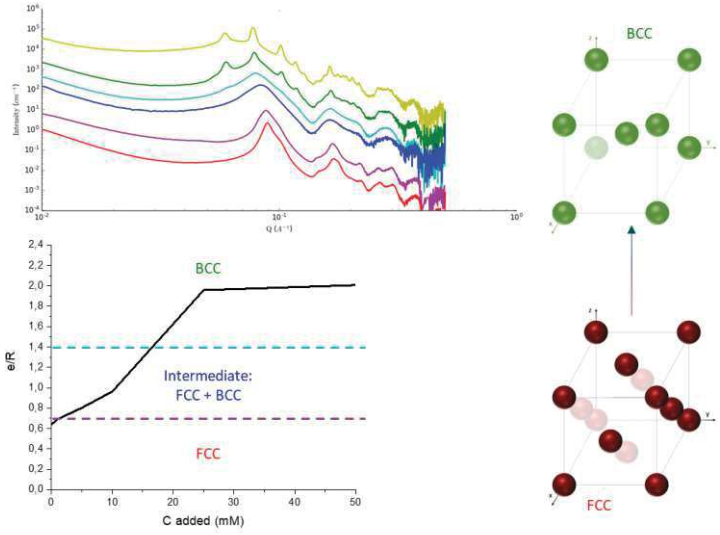

Fig. 1 Evolution of gold nanoparticle superlattice structure from FCC to BCC as a function of an excess of ligand: a. SAXS diagram, b. phase diagram, c. schematics of the structures.

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Hydrogen evolution reaction by transition metal complexes with redox-active ligands

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Facing the 21st century energy challenge, hydrogen production as an alternative fuel by catalytic water splitting is a central theme in the field of renewable energy storage. Platinum possesses the best performances among catalysts able to reduce protons to hydrogen. However, due to its scarcity and its cost, efforts to find alternative non-noble transition metal catalysts have been the subject of intense research.[1] A number of molecular catalysts based on Earth-abundant metals have been developed in the recent years. Together with the introduction of proton relays in the second coordination sphere of the metal center, redox-active ligands can be exploited to promote or enhance catalytic activity. Transition metal complexes with thiosemicarbazone ligands have been studied for many years as these complexes present some interesting features (redox properties, nitrogen or sulfur atoms as potential proton relays) for hydrogen evolution. In that perspective, we have associated the electroactive thiosemicarbazone ligand with redox-active transition metals like nickel,[1,4] palladium[2] and cobalt.[3] We have reported on the experimental and theoretical characterization of the complexes as well as their evaluation as electrocatalysts for proton reduction in an effort to rationalize the influence of the metal center on the catalytic performances.[5]

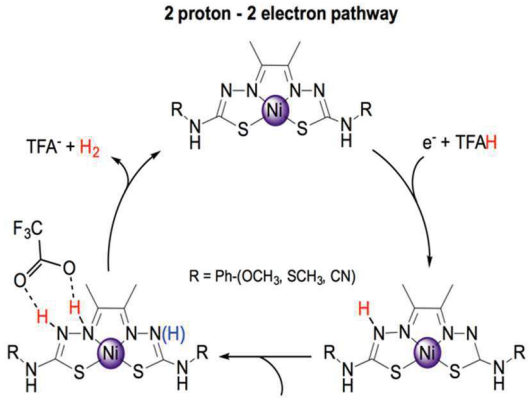

Figure 1. Hydrogen evolution reaction with thiosemicarbazone nickel complexes

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Les complexes 3d en géométrie bipyramide pentagonale : des briques uniques pour le magnétisme moléculaire

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La géométrie bipyramide pentagonale (symétrie D_{5h}) peut être induite dans certains complexes heptacoordinés par l'utilisation de ligands pentadentate (Figure 1). Ces ligands planaires comportent des sites de coordination variés N_5, N_3O_2 ou N_3S_2 permettant de moduler le champ de ligand équatorial tandis que les positions axiales peuvent être substituées sans altérer la géométrie du métal. Ces modifications ont un impact plus ou moins prononcé sur l'éclatement orbitalaire du métal. Certaines configurations électroniques sont anisotropes magnétiquement et de telles variations énergétiques des orbitales ont alors une répercussion sur l'anisotropie ce qui conduit dans certains exemples à des comportements de type aimants moléculaires.

Le choix des substituants périphériques du ligand offre une large famille de composés qui peuvent être connectés *via* des ponts cyanure pour former des systèmes hétérométalliques. Ces groupements permettent d'une part de contrôler les espèces cristallisées (discrètes ou 1D) et d'autre part d'ajouter des propriétés additionnelles, par exemple optiques avec des groupements chiraux. Enfin, nous verrons que les complexes de Fe^{II} ont des spécificités propices à la préparation des SMMs et SCMs.

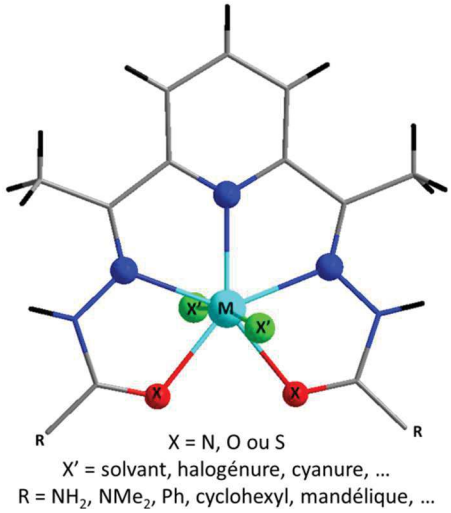

Figure 1. Représentation des complexes heptacoordinés

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Ferrocene : a versatile building block for polymerization under visible to NIR lights

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Ferrocene; push-pull, chalcone, photopolymerization, visible light, NIR

The shift towards higher actinic wavelengths in light induced reactions is a constant challenge in many academic/industrial works. During the last decade, the use of visible light in photoredox catalysis instead of harmful UV irradiations allowed significant advances in i) the selectivity of the photoreaction and ii) in the harmfulness of the actinic setup. Particularly, visible light-emitting diodes (LED) and laser diodes (LD) with their sharp emission spectra allows taylor-made light absorption by photoredox catalysts. Nevertheless, photoredox catalysis – partial and convenient regeneration of the catalyst – remained mostly restricted to actinic lights below 700 nm. Indeed, near infrared (NIR) induced photoredox catalysis remains an old dream which is particularly difficult to achieve as a NIR photon at 900 nm is three times less energetic than a UV one at 300 nm. Out of the challenge, there is a real interest in using NIR wavelengths: it offers several advantages such as an excellent penetration in filled, dispersed or even heterogeneous samples, and a higher selectivity of the photoreaction as the process is less energetic.

In this presentation, an overview of the different photoinitiating systems incorporating ferrocene as a photocatalyst will be presented. Over the years, ferrocene has been introduced in various structures such as push-pull dyes, in bio-inspired photoinitiators based on the chalcone structure, the design of benzophenone-derived structure. As a result of this diversity of structures, ferrocene derivatives are now capable to initiate polymerization processes from the visible range to the near-infrared range.

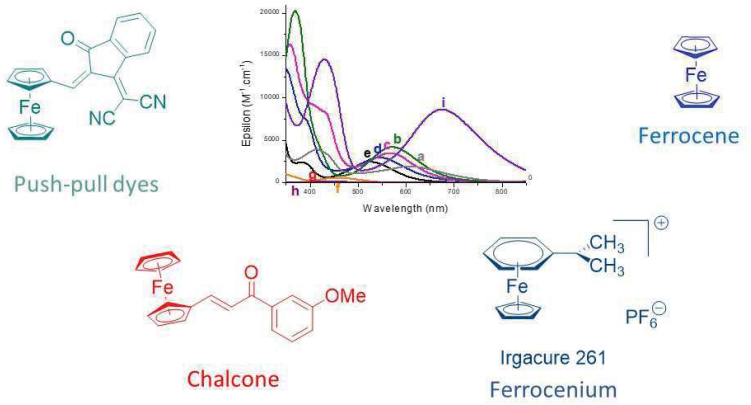

Fig. 1 Examples of ferrocene-based photoinitiators of polymerization.

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Fe/Co Prussian Blue dinuclear analogues: a new inside into the metal-to-metal electron transfer phenomenon

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Keywords: metal-to-metal electron transfer; molecular Fe-CN-Co Prussian Blue analogues

Switchable materials changing their physical properties under external stimuli such as light, temperature or magnetic field, are of huge interest in molecular information storage.[1] Molecular Fe/Co Prussian blue analogues (PBAs) are valuable examples of such systems exhibiting thermo- and photo-induced intra-molecular metal-to-metal electron transfer: $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\} \leftrightarrows \{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{LS}\}$ (LS = low spin; HS = high spin).[2] Since the discovery by the Hashimoto's group of the first photoswitchable Prussian blue analogue, $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$,[3] different molecular PBAs of different nuclearities have been reported: cubes $\{Fe_4Co_4\}$,[4] squares $\{Fe_2Co_2\}$[5] to the smallest elementary moiety, $\{FeCo\}$[6]. The appropriate selection of the blocking ligands on the donor (Co^{II}) and acceptor (Fe^{III}) sites allows a fine tuning their redox potential and thus, of the metal-to-metal electron transfer process. In this work, we will discuss on synthesis, magnetic and electrochemical properties of the smallest Fe/Co PBA units and how diamagnetic $\{Fe^{II}(\mu\text{-}CN)Co^{III}\}$ and paramagnetic $\{Fe^{III}(\mu\text{-}CN)Co^{II}\}$ complexes can be obtained by optimizing the respective blocking ligands.

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Effect of Substituents Mimicking Anchoring of Rhenium Carbonyl Bipyridine Molecular Catalysts for CO_2 Electroreduction

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Keywords: Rhenium carbonyl complexes, spectroelectrochemistry, catalysis of CO_2 reduction

The electrochemical reduction of CO_2 is a domain of intense activity with the aim to use CO_2 as a source of carbon for fuels or, more broadly, for commodity molecules. Efforts are thus made to develop selective catalysts for CO_2 electroreduction. In that endeavor, the advantage of molecular catalysts is that their structure and properties can be precisely controlled. Molecular compounds are usually studied as homogeneous catalysts to evaluate their figure of merits.[1] However, moving forward to applications, it is often better to design systems in which molecular catalyst are heterogenized on the electrode (or photoelectrode) surface.[2] Different strategies have been developed to immobilize molecular catalysts on conductive surfaces, including the direct chemical bonding which the advantage is the linkage robustness. Among the variety of molecular linking groups phosphonate and carboxylate chemical functions can be used. When the catalyst is a transition metal complex, one of these anchoring groups has to be connected to the complex through the ligands and an important question is thus raised on its influence on the redox properties and on the catalytic properties of the complex. Although the role of substituents present on ligands of molecular catalysts has been studied in many cases,[3] the question of the effect of anchoring groups has not been specifically reported.

Herein we will illustrate this issue through the detailed investigation of rhenium triscarbonyl bipyridine (bpy) complexes. We show that the presence of methoxycarbonyl groups on the bpy, used as a mimic for covalent attachment of the Re complex on a substrate, dramatically decrease the activity of the complex toward CO_2 electroreduction. A detailed study combining cyclic voltammetry and spectroscopies reveals the underlying reasons for such a drastic effect. Then, we show that using different mimicking anchoring groups, such as diethylmethylphosphonate ester groups not conjugated with the bpy ligand, allows preserving the catalytic activity toward CO_2 electroreduction.

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Synthesis and Encapsulation Properties of Porphyrin Cages Assembled from N-heterocyclic Carbene-Metal Bonds

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Keywords : Porphyrins; Carbenes; Self-assembly; Cofacial porphyrin dimers; Host-guest chemistry

N-heterocyclic carbenes (NHCs) and porphyrins have become ubiquitous ligands in the fields of organometallic chemistry and catalysis.[1] Over the last decade, NHCs have also emerged as promising ligands for the synthesis of metallosupramolecular architectures featuring M–C_{NHC} bonds.[2] For this purpose, numerous poly-NHC ligands were reported in the literature allowing the formation of discrete assemblies of various sizes and shapes. Here, we show that porphyrins equipped with imidazolium salts on the *para* positions of the four *meso* aryl groups can be used as NHC precursors for the synthesis of porphyrin cages assembled from eight M–C_{NHC} bonds.[3] Silver(I) was used as assembling metal ions because they form labile bonds with NHC ligands enabling the formation of thermodynamic products which are self-assembled porphyrin dimers with a face-to-face orientation. Moreover, the lability of Ag(I)–C_{NHC} bonds offers the possibility to generate new structures by transmetalation reactions forming more stable bonds like Au(I)–C_{NHC} with retention of the metallosupramolecular structures. Host-guest chemistry is feasible with porphyrin cages incorporating flexible linkers between porphyrins and NHC ligands. Indeed, the inner space between the two porphyrins of these cages expands enough to allow the encapsulation of guest molecules like water molecules or 1,4-diazabicyclo[2.2.2]octane (DABCO).[4]

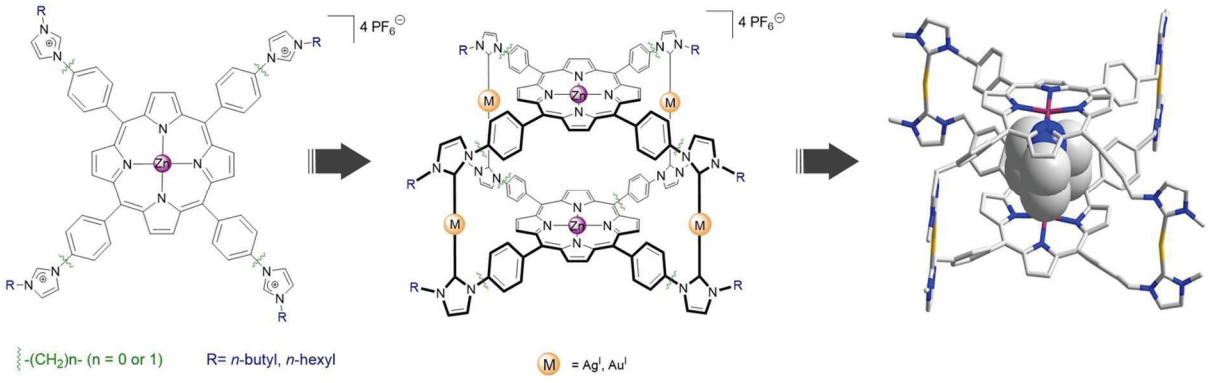

Fig. 1 Left: porphyrin-NHC precursors. Middle: cofacial porphyrin dimers. Right: DABCO molecule encapsulated in a cofacial porphyrin dimer.

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Trifluoromethylation through Ag(I)/Ag(III) Redox Manifold

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Keywords : Ag^{III} Chemistry; cross-coupling; fluorine; high-valent species; trifluoromethylation.

Texte:

Despite their widespread use in many transformations as additives or co-catalysts, silver compounds are generally believed to not interfere with the main metal reactivity and their potential as cross-coupling promoters has long been overlooked. This is most likely due to the erroneous belief that Ag is incapable of undergoing 2*e*⁻ redox processes. We first targeted the easy access to the organosilver(III) compound $[Ag^{III}(CF_3)_4]^-$ (**1**), thus bridging the possibility to explore the Ag(III) reactivity in depth. The original Naumann's method for the synthesis of **1** was reported back in 1986, and required the use of $Cd(CF_3)_2$ (toxic and explosive) as transmetallating agent leading to $[Ag^{I}]^+[Ag^{III}(CF_3)_4]^-$ (**Ag-1**) in modest yield (25% *vs.* initial Ag(I) salt)[1]. In 2018 B. Menjón revisited this chemistry, and found an alternative two step synthesis of $[PPh_4]^+[Ag^{III}(CF_3)_4]^-$ (**PPh_4-1**) through intermediate formation of $[PPh_4]^+[Ag^{I}(CF_3)_2]^-$ and the following oxidation with $PhI(OAc^F)_2$. Yet the yield of **1** was still restricted to 30% and the use of costly and hazardous reagents was mandatory[2]. We herein report the aerobic oxidation of AgF in presence of KF and CF_3TMS giving rise to $[K]^+[Ag^{III}(CF_3)_4]^-$ (**K-1**)[3] safely, in high yield and in multigram scale. The neutral compounds $[(bpy)Ag^{III}(CF_3)_3]$ (**2**) and $[(phen)Ag^{III}(CF_3)_3]$ (**3**) where synthetized via α-fluorine elimination, and mechanistic investigations revealed the crucial role of the K^+ cation. The utility of **3** in cross-coupling reactions has been unambiguously proven. In particular, **3** underwent the trifluoromethylation of a large variety of arylboron compounds in presence of a base and in aqueous media. The reaction proceeds through the intermediate formation of $[Ag^{III}(aryl)(CF_3)_3]^-$ complexes via boron-to-Ag^{III} aryl transfer, and the subsequent reductive elimination and C–CF_3 bond formation. In short, the elementary steps required to implement Ag^{I}/Ag^{III} redox catalysis were investigated (**Fig. 1**), and definite proof was provided for: *i)* easy Ag^{I}/Ag^{III} 2*e*⁻ oxidation mediated by oxygen; *ii)* bpy/phen ligation to Ag^{III}; *iii)* boron-to-Ag^{III} aryl transfer; and *iv)* reductive elimination of benzotrifluorides from well-defined aryl-Ag^{III}-CF_3 complexes. These findings have demonstrated the ability of high-valent Ag^{III} to accomplish a given cross-coupling reaction via a 2*e*⁻ pathway by itself, without relying on a second metal additive. This subverts old stereotypes and misconceptions about the assumed chemical inertness of silver compounds for C–C bond formation and its limitation to 1*e*⁻ reaction pathways.

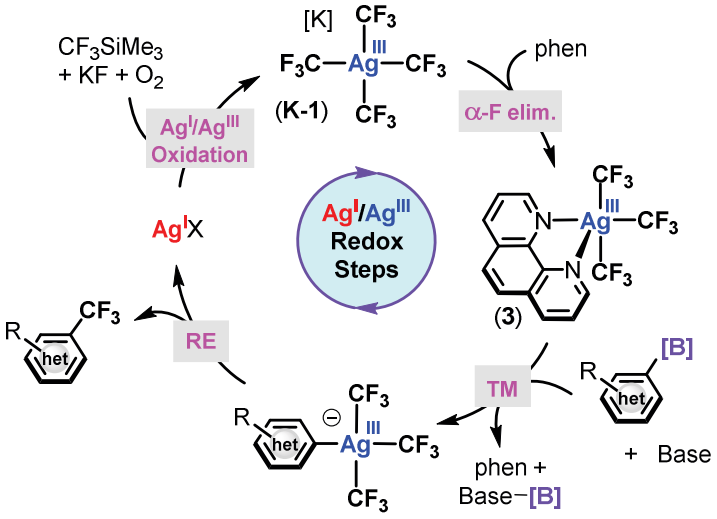

Fig. 1: Mechanistic depiction for the oxidative trifluoromethylation of arylboron derivatives via Ag^{I}/Ag^{III} redox shuttles.

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Organometallic chemistry of low-valent lanthanides: unusual oxidation states and magnetic sandwiches

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Organometallic complexes of f-elements are an interesting class of organometallic compounds developed in the 1950s and now concern most of the rare earth ions in their trivalent and divalent states as well as many of the actinides. The applications for such compounds are numerous for single electron transfer reactivity[1] and small molecules activation[2]. Because of their optical and magnetic properties, their Single-Molecule-Magnet behavior has impressed with record blocking temperatures.[3] Additionally, very original magnetic behaviors have shed light on their intriguing bonding nature.[4] We will present a short overview of our methodology for synthesizing organometallic complexes with the very original geometry.[5] The oxidation state is not trivial to assess because of the development of intermediate valent electronic states.[6] The magnetic data is used as a guide for a better understanding of their bonding and has led to the report of several compounds featuring SMM properties.[7]

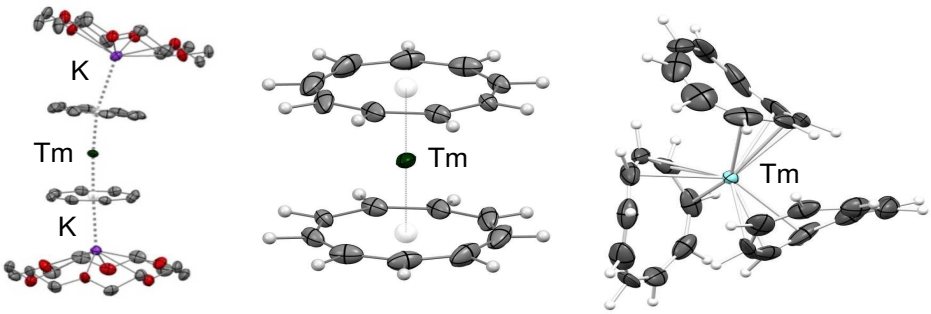

Figure: *Tm organometallic complexes with the Cot (cyclooctatetraenyl) and the Cnt (cyclononatetraenyl) ligand.*

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