

CHAOTROPIC EFFECT AS MOTIF ASSEMBLY IN POM CHEMISTRY

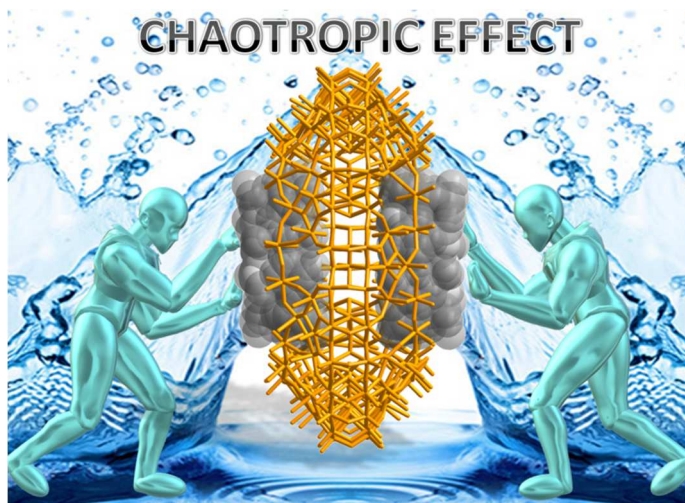
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Following up on reports on interactions of conventional chaotropic anions (SCN^- , ClO_4^- ...) with non-ionic organic entities (proteins, macrocyclic hosts, micelles...), the chaotropic effect has recently emerged as a generic driving force for supramolecular assembly. This water-mediated effect becomes extremely effective for large inorganic polyanions such as the polyoxometalates (POMs) which are appealing metal–oxo clusters for applications in catalysis, medicine or energy storage and conversion.

This talk will review our recent findings demonstrating the mastering of the chaotropic effect offers innovative avenues i) to control the polycondensation of metalate ions,^[1,2] ii) to design redox-responsive host-guest systems,^[3,4,5] iii) to construct highly ordered hybrid systems with large cavities, and iv) to self-assemble POM with non-ionic surfactants into membrane-like organizations.



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À propos des phosphures ambiphiles

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Mots-clés: phosphore; liaison chimique; formalisme de la flèche; synthèse template; bimétalliques

Les composés de phosphore divalent à couche fermée sont généralement classés soit comme des anions phosphures nucléophiles (PX_2^-), soit comme des cations phosphéniums électrophiles (PX_2^+). L'influence des substituants X peut cependant brouiller la frontière entre ces deux classes de composés en leur conférant un caractère ambiphile. Si les exemples de phosphéniums ambiphiles (par ex. **A**, **B**) sont relativement répandus, les phosphures ambiphiles (par ex. **C**) constituent une classe de composés beaucoup plus restreinte.¹ Nous avons récemment décrit l'utilisation de bis(iminophosphoranyl)phosphures (**BIPP**) comme ligands pour les métaux de transition. Malgré leur charge négative, les **BIPP** peuvent être décrits comme des triphosphéniums (**TP**) électroniquement enrichis — donc comme des phosphures ambiphiles. L'emploi du formalisme de la flèche permet de saisir l'analogie entre **BIPP** et **TP** d'une part, et de rendre compte de leur réactivité comme sources de « P^+ » d'autre part ; cependant ce formalisme ne correspond pas à la nature covalente classique de la liaison P-P, il doit donc être employé avec circonspection.² Pour finir, nous montrerons comment la réactivité des **BIPP** peut être exploitée pour la synthèse template de nouveaux ligands phosphures de type « pince » et de complexes hétérobimétalliques Ti/Rh et Ti/Ir (Fig 1).³

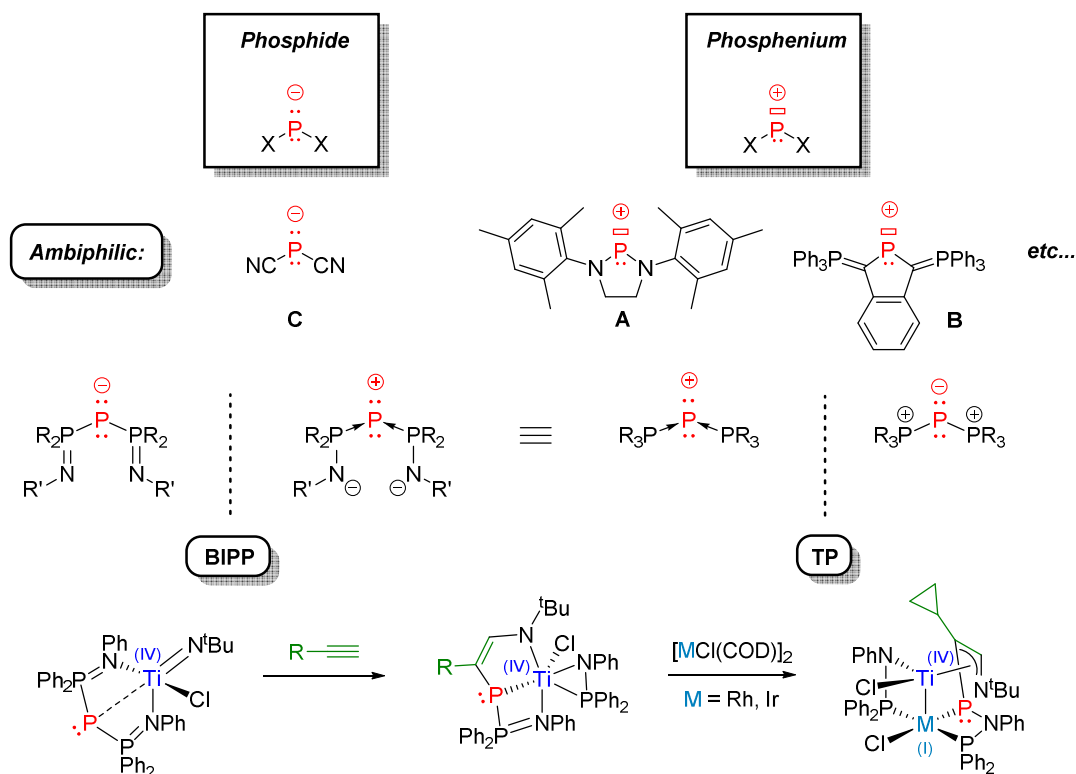


Fig. 1

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COOPERATIVE REACTIVITY AT POLARIZED HETEROBIMETALLIC PAIRS

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Keywords : heterobimetallic complexes, iridium, hydrides, CO₂ activation, C-H activation, surface organometallic chemistry

Texte: One of the current frontiers in organometallic catalysis is to study the combined action of two metal centers to promote novel modes of reactivity, where the two metal centers act in synergy, in order to access a chemistry not possible with monometallic species. The association of electron-rich late metal centers (such as iridium), with Lewis acidic metals (such as aluminium or tantalum) is particularly interesting to create strongly polarized metal-metal pairs presenting original electronic structures, and thus potentially novel reactivity. Recently, we have shown that these polarized heterobimetallic pairs are able to activate carbon dioxide (Figure 1a)¹ as well as C-H bonds (Figure 1b)²⁻⁴ in a concerted way on both metal centers, which explains why these bimetallic systems have a catalytic activity largely superior to their monometallic analogues. In this communication we will describe our latest results in this area of research.

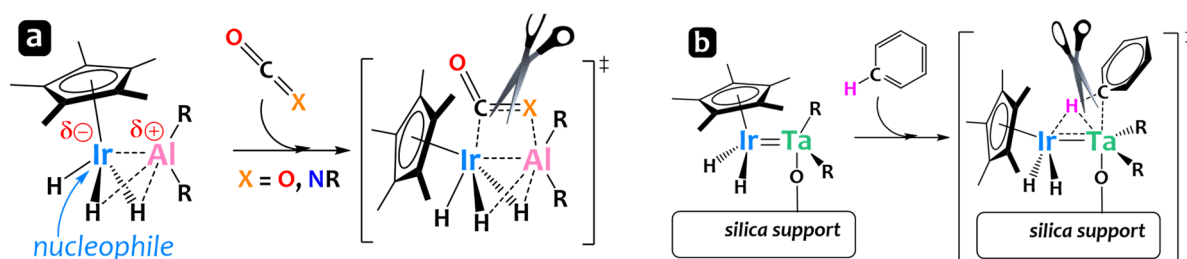


Fig. 1 Reactivity of heterobimetallic complexes for the activation of CO₂ or C-H bonds by original cooperative mechanisms across the two metals.

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NHC and Phosponium Ylides: A Fruitful Association in Coordination Chemistry

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Keywords: Carbon ligand, NHC, phosphonium ylide, metal complex, homogeneous catalysis.

Among the large variety of ligands available, carbon ligands have become essential, especially with the emergence of N-heterocyclic carbenes (NHCs), positioning themselves as valuable alternatives to N-, and P-based ligands. Phosponium ylides, which represent a complementary class of neutral carbon ligands were also demonstrated to act as effective Lewis bases in main-group and coordination chemistry. Considering the intrinsic features of the carbene and phosphonium ylide ligands, similar in terms of electronic properties, but different in terms of bonding mode, the development of hybrid systems combining both carbon functionalities appeared as a natural challenge. On the basis of these findings, these two strongly donating carbon moieties were associated in different ways over the years (Fig. 1).¹

Thus, these two carbon donors can either interact as in species of type **A** where one fragment acts formally as the substituent of the other,² or simply occupy remote positions separated by an insulating linker to afford chelating ligands of type **B** where each donor retains its own electronic and steric features.³ These different systems associating carbenes and ylides will be discussed from fundamental aspects to catalytic applications.

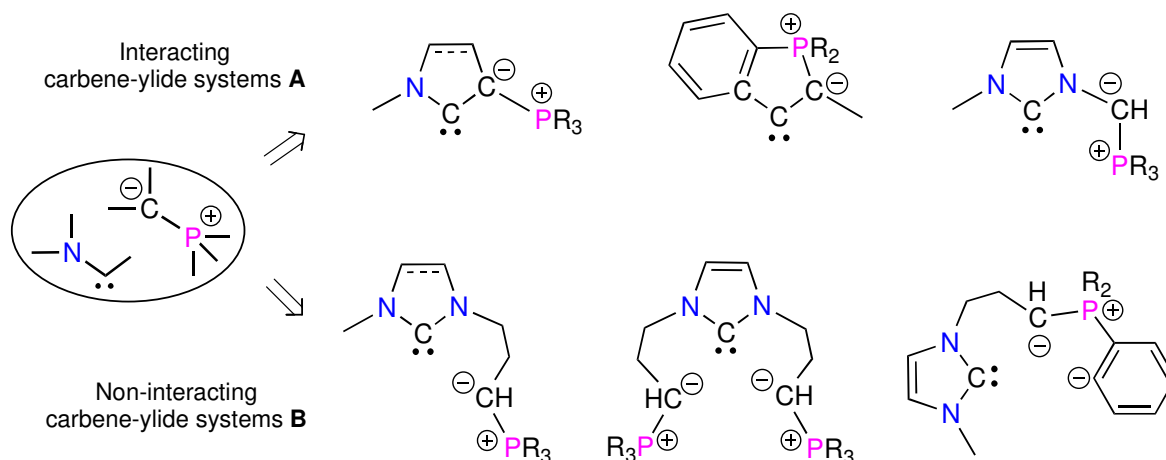


Fig. 1 Representation of known systems **A-B** associating carbene and phosphonium ylide donors with more or less interaction between them.

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MÖBIUS Zn(II) HEXAPHYRIN COMPLEXES WITH SWITCHABLE CHIRALITY

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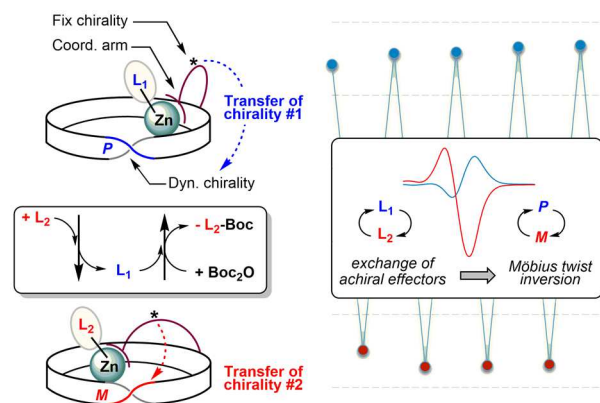
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Keywords : Chiroptical properties; Dynamic chirality; Molecular recognition; Möbius aromaticity; Porphyrinoids; Zinc complexes

Among the various types of chirality (central, axial, helical, planar...), that inherent to Möbius topology remains almost unexplored, partly due to the difficult access to Möbius compounds.¹ Considering the paramount importance of chirality in biological processes, drug design, material sciences and many other fields, scrutinizing Möbius chirality could benefit to a large community of researchers. Currently, the asymmetric preparation of Möbius compounds remains challenging. One strategy relies on stereochemically stable Möbius ring, only two examples being described in the literature.² Focusing on the Möbius [28]hexaphyrin scaffold, our group has investigated a different approach for chirality induction taking advantage of the dynamic character of the twisted π system.³ Indeed, this scaffold is conformationally flexible and undergoes rapid $P \leftrightarrow M$ equilibrium in solution, thus exhibiting a dynamic Möbius chirality. This feature enables a transfer of chirality from an exogenous stereogenic source under thermodynamic control, useful to build up adaptive systems. Möbius Zn(II) metallo-receptors exhibiting a strong interplay between aromaticity, guest recognition, and chirality transfer have been revealed, opening a new playground.

Recently, we have extended our dynamic approach to a different situation, where a source of fix chirality is part of a covalently attached coordinating arm, leading to the following main findings: (i) both



Möbius configurations are reached *in-situ* by simple addition of suitable achiral effectors tuning the way a fix stereogenic source interacts with the ring. Impressive stereoselectivities (diast. excess > 95%) highlight the most efficient transfer of chirality to a Möbius ring reported so far; (ii) these achiral effectors generate distinct chiroptical states featuring electronic circular dichroism spectra with bisignate Cotton effect of opposite signs. Switching between these two states owing to ligand exchange was successfully achieved with high robustness using a chemical trigger (10 cycles).^{3f}

Fig. 1 Working principle of a Möbius-type chiroptical switch.

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Weak-field coordination of a new iron(0) adduct with an exceptional thermal stability : electronic properties and cycloaddition catalytic activity

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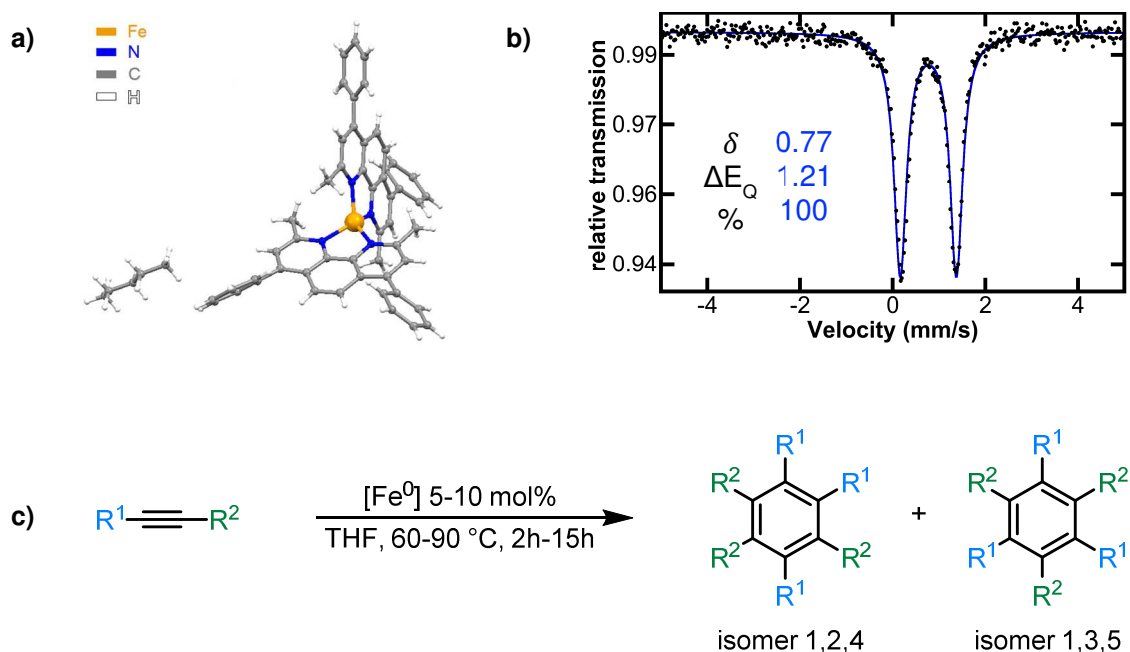
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Keywords : iron; catalysis; trimerization.

We report the synthesis of new iron(II) and iron(0) complexes stabilized by a sterically bulky phenanthroline derivative.¹ Unlike the single previous example of such kind of iron complexes,^{2,3} these species have been found to be extremely stable regarding time as well as temperature, and the iron(II) complex is air insensitive. Both species are fully characterized by paramagnetic ¹H NMR, SQUID, elemental analysis, X-ray diffraction, magnetic circular dichroism and Mössbauer spectroscopy (Scheme 1, a and b). The thoughtful study of iron(0) electronic structure also revealed, to a certain extent, a non-innocent behavior. Besides, reactivity of the iron(0) complex is investigated through iron-catalyzed alkyne trimerization reactions (Scheme 1, c). Trimerization of several alkynes, either internal or terminal, and cross-cycloaddition using diyne compounds are performed with excellent results in terms of yield and regioselectivity.

Scheme 1: single-crystal X-ray diffraction structure (a), ⁵⁷Fe-Mössbauer spectrum (b) and catalytic activity (c) of the iron(0) complex.



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Synthesis and reactivity of diphosphine NHC-borane compounds

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Keywords : NHC-borane; Phosphine; Transition-metal coordination

NHC-boranes are robust Lewis adducts and powerful reagents as hydrogen atom and hydride donors.¹ Comparatively, their coordination chemistry is quasi-unknown since only one report described it in 2010.² This feature might be explained by the instability of such a construction.

Aiming at studying the coordination chemistry of NHC-borane with transition metals as well as the possible B-R bond activation, we targeted NHC-borane structure featuring two-electron donor ligands to serve as anchor of coordination.

Using a known diphosphine carbene platform,⁴ we prepared NHC-borane species featuring two pendant phosphine moieties in order to target bimetallic structures. Indeed, homogeneous multi-metallic systems are powerful materials to achieve cooperative effects otherwise unreachable by their monometallic counterparts, as exemplified by heterogeneous surfaces and metallo-enzymes.³

In this presentation, we will discuss the synthesis and characterization of such original organoboron compound. We will also describe its use as ligand for transition metals with a special focus on the different hapticities encountered.

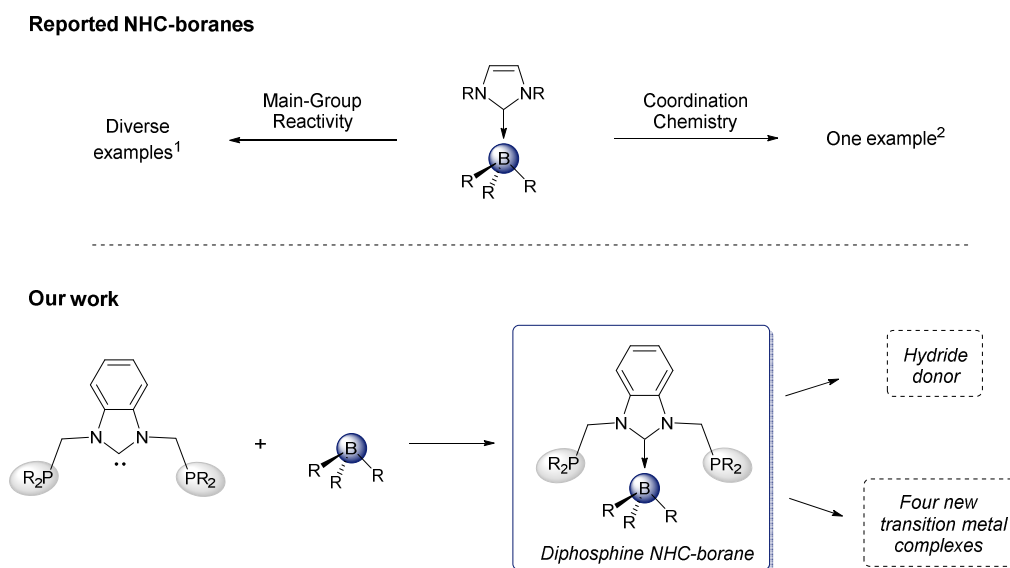


Fig. 1 Synthesis of a new NHC-borane scaffold and reactivity in main-group and coordination chemistry

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Molecular electrochemical CO₂ catalytic reduction to C₁ products with 2, 4, 6 and 8 electrons with Co and Fe complexes

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Keywords : CO₂ reduction; molecular catalysis; electrochemistry

Electrochemical reduction of carbon dioxide (CO₂) to carbon monoxide (CO) and other C₁ products under mild conditions puts us on the trail of a new way to produce fuels and chemical feedstock. To achieve these processes, molecular catalysts made of Earth-abundant metals are the seat of our research, offering a variety of operating conditions (homogeneous vs. supported heterogeneous catalytic systems).

Co and Fe complexes demonstrate excellent conversion of CO₂ to CO with a selectivity reaching 99 %, in organic solvent as well as in water. By setting proper conditions, we recently discovered that formaldehyde and methanol (Co complex) as well as methane (Fe complex) could be obtained. In other words, CO₂ could be reduced with 2, 4, 6 and 8 electrons with molecular catalysts. These results highlight the role of metal-based catalysts' environment in obtaining of reduction products beyond two electrons. Our most recent results will be presented.

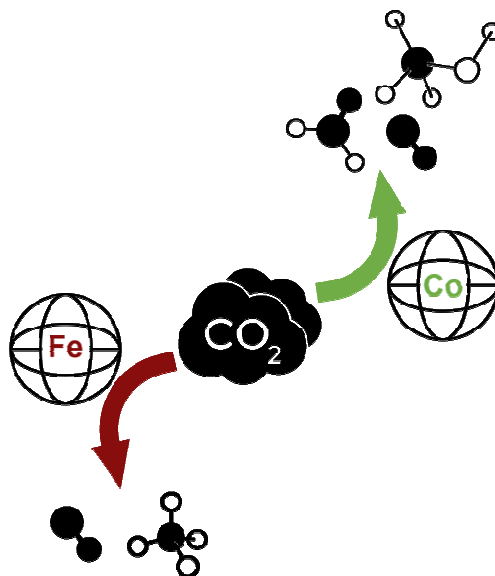


Fig. 1 CO₂ reduction to CO and other C₁ products: formaldehyde and methanol for the Co complex, methane for the Fe complex.

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Association of polyoxothiometalate with cyclodextrins: Host-guest complex and supramolecular open frameworks

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Keywords : Polyoxothiometalate; Cyclodextrin; Supramolecular chemistry; X-ray structure

Designing a new class of responsive and adaptable multifunctional materials built from deliberate supramolecular interactions is promising for a large variety of applications (e. g. drug delivery, gas sorption, sensors, etc.). In 2015, the group of Prof. F. Stoddart evidenced the remarkable affinity between the cyclodextrins and polyoxometalates (POMs).¹ Since this pioneered work, our research group has exploited such association, which is mostly governed by chaotropic effect, to i) control metalate condensation processes, ii) construct hybrid open frameworks, or iii) redox-responsive host-guest systems.^{2,3,4} In this communication, we will explore the supramolecular systems based on polyoxothiometalates (ThioPOM), a preformed inorganic molecules recognized for their HER catalytic properties, and cyclodextrins.

First, we will show that the assembly of β -CD and $[\text{Mo}_8^{\text{V}}\text{Mo}^{\text{VI}}\text{O}_8\text{S}_8(\text{OH})_9(\text{H}_2\text{O})]^{3-}$ lead to a 1:2 host guest compound characterized by ^1H NMR in solution and single-crystal X-ray diffraction in the solid state (see Figure). Then, we will demonstrate how the situation differs dramatically when α -CD is employed. Actually, the self-assembly between the discoidal ThioPOM and the organic macrocycle, promote the formation of well-defined 3D network exhibiting a Kagome lattice. Remarkably, this supramolecular open framework reveals the presence of large cavities (see Figure). Finally, we will discuss the adsorption properties of this hybrid solid.

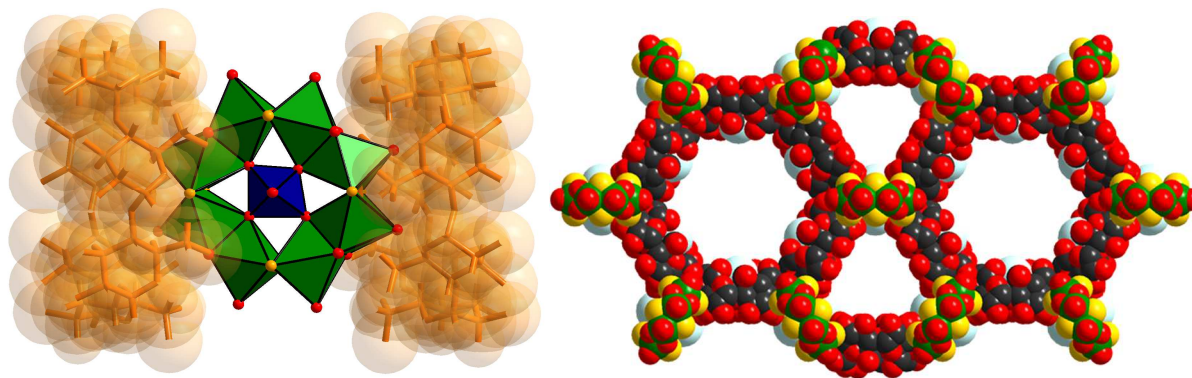


Fig. 1 Left side – Structural representation of the host-guest interaction in $\text{K}_3[\text{Mo}_9\text{O}_8\text{S}_8(\text{OH})_8(\text{H}_2\text{O})]@\beta\text{CD}_2$. Right side – $\text{K}_3[\text{Mo}_9\text{O}_8\text{S}_8(\text{OH})_8(\text{H}_2\text{O})]@\alpha\text{CD}_2$, ball and stick representation.

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Metal Acetylacetonate–Bidentate Ligand Interaction (MABLI) (Photo)activated Polymerization: Toward High Performance Amine-Free, Peroxide-Free Redox Radical (Photo)initiating Systems

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Copper complex; phosphine; redox polymerization

Metal Acetylacetonate–Bidentate Ligand Interaction (MABLI) constitutes a new chemical mechanism for the highly efficient generation of free radicals for polymer synthesis. This MABLI process involves simultaneous ligand exchange and a change of the metal oxidation degree and is associated with the efficient release of free radicals. In conventional redox two-component radical generating systems, two criteria are required to be efficient: (1) oxidizing agents must exhibit a low bond dissociation energy (BDE) i.e. they are usually unstable (e.g. peroxides) and (2) a small difference must exist between the oxidation potential of the reducing agent and the reduction potential of the oxidation agent.

In contrast, here, the criteria for efficient MABLI radical generation are energetic and geometric for both bidentate ligands and metal acetylacetonates. The strength of this approach is to use stable compounds in 2-components free radical initiating systems and to generate carbon centered radicals.

In this presentation, recent developments concerning the MABLI approach will be presented.¹

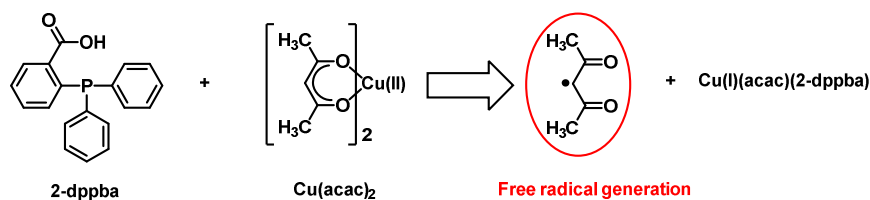


Fig. 1 Mechanism involved in the MABLI process.

1. Garra, P.; Dumur, F.; Nechab, M.; Morlet-Savary, F.; Dietlin, C.; Graff, B.; Doronina, E.P.; Sidorkin, V.F.; Gigmes, D.; Fouassier, J.-P.; Lalevée, J. *Macromolecules* **2018**, *51*, 6395–6404.

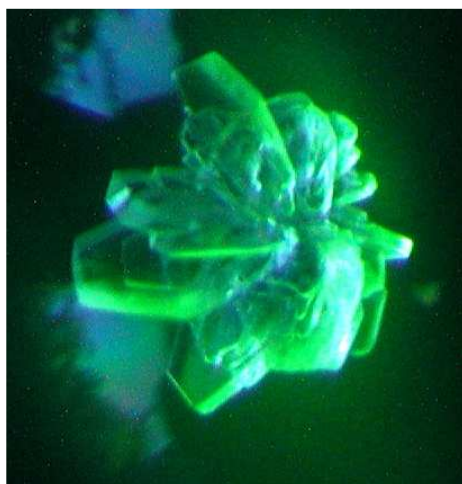
Versatile applications of a terbium complex.

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The sensitization of lanthanide luminescence by nonlinear two-photon (2P) absorption process is nowadays a well-established field of research able to combine the intrinsic advantages of rare earth spectroscopy (line shape emission with large Stokes shift, long lifetime) and those of biphotonic microscopy (NIR excitation, 3D resolution,...) for bio imaging purpose.¹ In this context we reported a family functionalized triazacyclononane ligands leading to the formation of ultra-bright Eu, Tb, Yb, Sm(III) complexes featuring optimized brightness.² In marked contrast the use of lanthanide as additive to assist the protein cristallisation process is an emerging application opening a fascinating field of research.

We recently discovered the potentialities of a new terbium complex called *crystallophore* and described its use as powerful nucleating agent.³ Here we will present a new derivative combining nucleating ability and two-photon imaging properties to image micro-crystals properties.



1. For a review see : C. Andraud, O. Maury *Eur. J. Inorg. Chem.* **2009**, 4357.

2. A.-T. Bui, A. Roux, A. Grichine, A. Duperray, C. Andraud, O. Maury *Chem. Eur. J.* **2018**, *24*, 3408-3412

3. S. Engilberge, F. Riobé, S. Di Pietro, L. Lassalle, N. Coquelle, C. Arnaud, D. Madern, C. Breyton, O. Maury, E. Girard *Chem. Science.* **2017**, *8*, 5909-5917.