

# Synthesis and Luminescence of Chiral Lanthanide Complexes

Annika Sickinger, François Riobé and Olivier Maury

Laboratoire de Chimie, ENS de Lyon, 46 allée d'Italie 69364 LYON CEDEX 07  
annika.sickinger@ens-lyon.fr, www.ens-lyon.fr/CHIMIE

**Keywords:** Lanthanide complexes; chirality; circularly polarized luminescence

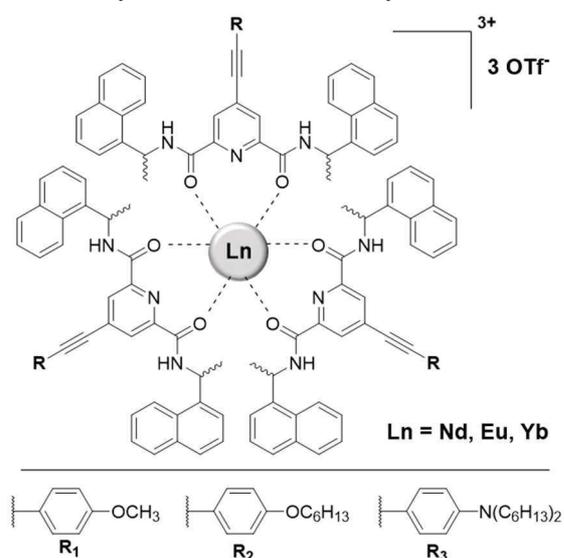
Lanthanide-based metalorganic complexes open up new possibilities in various fields of application, profiting from the unique, closely correlated magnetic and luminescent features which are enabled by their partially filled 4f valence shells. As the 4f transitions in isolated Ln(III) ions are, however, forbidden by symmetry rules, the presence of a coordinating sphere of suitable ligands is required to lift the degeneracy of ground and excited electronic states, thereby giving rise to distinct optical properties.<sup>1</sup> Moreover, the underlying crystal field interactions implicate the capacity to generate distinct magnetic anisotropies and allow for the application of Ln(III) complexes as single-molecule magnets.<sup>2</sup> As both optical and magnetic properties of metalorganic complexes are governed by their electronic structure, their understanding and tunability require profound knowledge on the corresponding crystal field splitting. Reversely, magnetic and luminescence measurements reveal in-depth insight into the electronic structure of the respective system.<sup>3</sup>

As has been demonstrated, the preparation of chiral Ln(III) complexes by careful ligand design enables the emission of circularly polarized light, as each of both enantiomers absorbs or emits photons preferentially with one sense of circular polarization.<sup>4</sup> Apart from the corresponding potential for applications like biosensing or anti-counterfeit devices, these features introduce additional selection rules for energetic transitions, thereby improving the discrimination of each contribution in absorption and emission spectra.

Initiated by studies on structurally related helical Yb(III) complexes, chelidamic acid based ligands with different conjugated antenna were synthesized.<sup>5</sup> The attached charge transfer functionalities were primarily chosen to ensure an efficient sensitization of the Ln(III) ions of interest. Apart from that, their increased polarity as compared to a previously investigated reference system (Ln = Yb, R = R<sub>1</sub>) is expected to facilitate the preparation of samples in polymer matrices required for the envisaged CPL measurements.

Depending on the ligands' stereochemistry, these wrap around the Ln(III) ion in the course of complex synthesis and induce either Λ- or Δ-type helical chirality. As a result, enantiopure complexes featuring luminescence in the UV/Vis (Ln = Eu) or in the near infra-red wavelength region (Ln = Nd, Yb) were obtained.

For all sets of complex enantiomers, extensive investigations by a combination of spectroscopic methods are anticipated. These include absorption and luminescence measurements as well as studies on circular dichroism and circularly polarized luminescence. Thus, the optical properties of the particular complexes are approached in both solid state and in solution, at room- and low temperature. In combination with magnetic studies and ab initio calculations, a detailed characterization of the electronic structure and the crystal field splitting of chiral Ln(III) complexes is envisaged.



**Fig. 1** Complexes of different lanthanide ions, coordinated by multidentate ligands with variable antenna function in a helicoidal fashion.

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# Reductive Depolymerization of Polyesters and Polycarbonates with Hydroboranes by Using a Lanthanum(III) Tris(amide) Catalyst

J.-C. Berthet, M. Kobylarski, and T. Cantat

LCMCE, IRAMIS, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France.

jean-claude.berthet@cea.fr; <https://iramis.cea.fr/Pisp/thibault.cantat/>

**Keywords** : Plastic, Chemical depolymerization, f-element, Hydroboration, Catalysis

Plastics are ubiquitous in our modern society and their world annual production now reaches 368 Mt and is expected to double in the next 20 years. Most household wastes accumulates in landfills or are burnt due to the absence of efficient and economical recycling and valorization processes.<sup>1</sup> Such a situation causes severe damage to the environment and emissions of large amount of CO<sub>2</sub>.<sup>2</sup>

The implementation of a circular economy of plastics lies on three main axes: drastic reduction of the leakage of wastes in the nature, the decoupling of plastic production from fossil resources and up-taking efficient recycling processes.

Today, while mechanical recycling is the most useful method to valorized plastic, the matter is however degraded by melting and most of the recycled polymer must be combined with virgin resins to retain the desired physical properties. Chemical recycling, which is the depolymerization of materials into valuable monomers useful for the production of recycled virgin quality plastics or chemicals for industry, now emerged as a long-term strategy complementary to mechanical recycling.<sup>3</sup> Some well-known catalytic methods have been developed for depolymerizing oxygen and nitrogen containing polymers such as the solvolysis processes (hydrolysis, aminolysis, alcoholysis). They offer the recovery of pure monomers useful for the production of new virgin plastics.

Recently, reductive depolymerization methods appeared as alternative approaches to access new value added products from plastics.<sup>4</sup> The goal is to develop catalytic systems able to selectively split and reduce polarized bonds of oxygenated (polyesters, polycarbonates and polyethers) and nitrogenated (polyamides, polyurethanes) polymers to obtain the corresponding monomers or some valuable derivatives (alcohols, amines or hydrocarbons).

Such ways are scarce. Hydrogenolysis methods require noble metals (Ru, Ir) and high pressure and temperature.<sup>5</sup> In contrast, the hydrosilylation of polyesters and polycarbonates took place under milder conditions with metal-based catalysts (Ir(III), Zn(II), Mo(VI)) or boron-based organocatalysts.<sup>4</sup> Surprisingly, hydroboranes reductants that could offer distinct reactivity and selectivity due to their higher hydride donor ability and additional pronounced Lewis acidity have never been tested.

Inspired by the work of T. J. Marks *et al.*<sup>6</sup> on the reduction of esters, we successfully used hydroboranes and the 4f-catalyst La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> to successfully depolymerize a wide range of polyesters and polycarbonates into their corresponding borylated alcohols (Fig.1).<sup>7</sup>

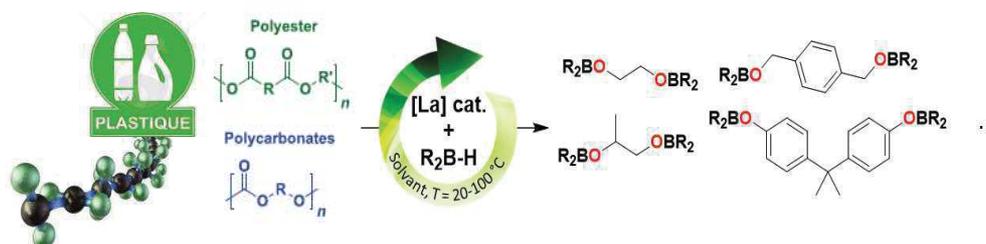


Fig. 1 Depolymerization of oxygenated plastics with the catalytic system La(III)/HBpin

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## Biphenyl-gold(III) scaffold: a new field of investigations for anticancer drug candidates

Benoît Bertrand,<sup>a\*</sup> Silva Khodjoyan,<sup>a</sup> Edwyn Remadna,<sup>a</sup> Héroïse Dossmann,<sup>a</sup> Denis Lesage,<sup>a</sup> Jérémy Forté,<sup>a</sup> Geoffrey Gontard,<sup>a</sup> Michèle Salmain<sup>a</sup>

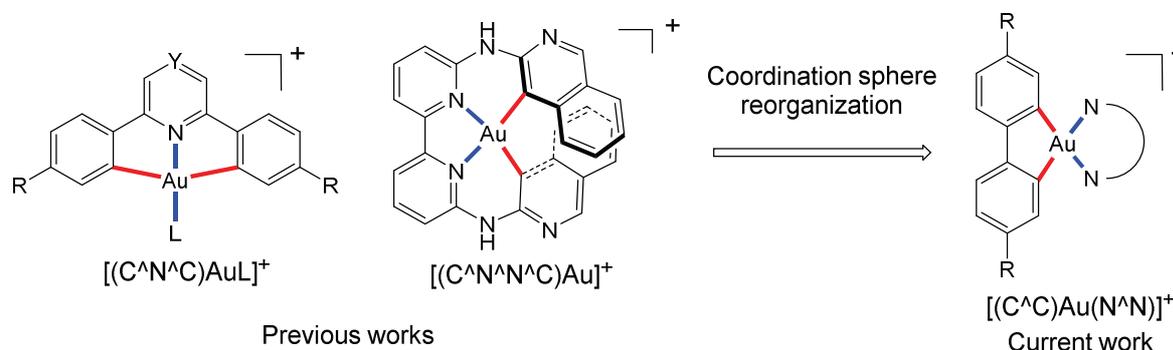
<sup>a</sup> Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire (IPCM UMR 8232), F-75005 Paris, France

adresse e-mail : [benoit.bertrand@sorbonne-universite.fr](mailto:benoit.bertrand@sorbonne-universite.fr),

webpage de l'institution : <https://ipcm.fr/article1322.html?lang=fr>

**Keywords** : gold, organometallic, chelate, cancer

Organometallic gold(III) complexes have attracted a large attention as potential anticancer agents in the last decades. The main advantage of organometallic complexes is their high redox stability in physiological media due to the presence of Au-C bonds. In this respect, bis-cyclometalated  $[(C^{\wedge}N^{\wedge}C)AuL]^+$  and  $[(C^{\wedge}N^{\wedge}N^{\wedge}C)Au]^+$  complexes have demonstrated great potential.<sup>1,2</sup> However, their main limitations are the large number of coordination site occupied by the pincer ligands leaving only one or no coordination sites for available for other ligands. Moreover, the amount of substitution tolerated on the pincer ligands are quite narrow meaning the possibility of variation of these scaffolds are quite limited. To enlarge the the scope of structures that can be tested and potentially explore new modes of actions while preserving the high redox stability of bis-cyclometalated complexes, a reorganization of their coordination sphere appeared as a promising potential. Using a biphenyl ligand giving two Au-C bounds would preserve the high redox stability of bis-cyclometalated complexes while offering two coordination sites available for various ligands to optimize the anticancer properties of the complexes. Our results on the synthesis and anticancer activity of biphenyl-Au(III) complexes presenting N- and P-donor ligands as anticancer agents will be presented.<sup>3</sup>



**Fig. 1:** Reorganization of the coordination of previously reported cyclometalated Au(III) complexes leading to the  $[(C^{\wedge}C)Au(N^{\wedge}N)]^+$  scaffolds.

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## Chiral stimuli-responsive metallo-supramolecular assembly induced by Cu<sup>I</sup>/Cu<sup>II</sup> redox change

C. Dussart, M. Marinova, A. Bonnefont., T. Achard,  
A. Maisse-François, S. Bellemin-Laponnaz

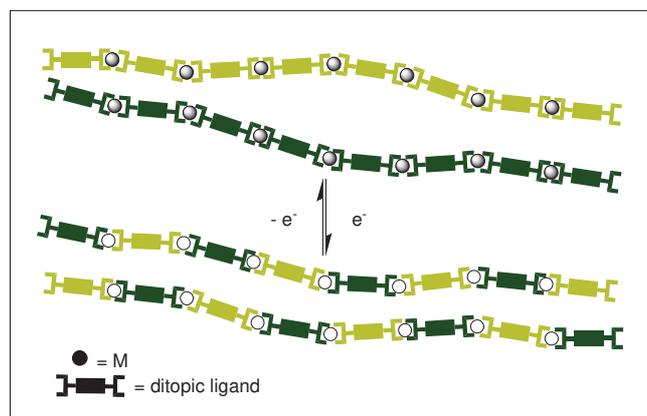
23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France  
caitlyn.dussart@ipcms.unistra.fr, www.ipcms.fr

**Keywords:** coordination chemistry, cyclic voltammetry, copper complexes, chirality, metallopolymers

### Texte:

Metallo-supramolecular polymeric assemblies are a new class of materials that has emerged in the last few decades.<sup>1</sup> These materials have a large range of properties depending on the nature of the metal centers and their ditopic ligands. The reversibility of their linkages can be used to do a supramolecular chiral recognition between enantiomeric molecules. This ability can lead to self-discrimination or self-recognition and generate pairs of enantiomers that are homochiral or heterochiral complexes.<sup>2</sup>

Our recent advances in this field will be presented.<sup>3</sup> We will describe how the Cu<sup>I</sup>/Cu<sup>II</sup> redox transition shows a chiral self-recognition or a self-discrimination through electrochemical studies. This phenomenon is also observed with the metallo-supramolecular copolymers, based on the ditopic version of these chiral ligands.



**Figure 1** Principle of the electrochemically-induced control of the metallo-polymer arrangement: generation of block or alternating metallopolymers through the selective formation of homoleptic (top) or heteroleptic complexes (down).

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## Synthesis and Characterization of New Hybrid Polyoxometalates for Photopolymerization Process

Z. El Hajj,<sup>a</sup> O. Oms,<sup>a</sup> S. Floquet,<sup>a</sup> P. Mialane,<sup>a</sup> et D.-L. Versace.<sup>b</sup>

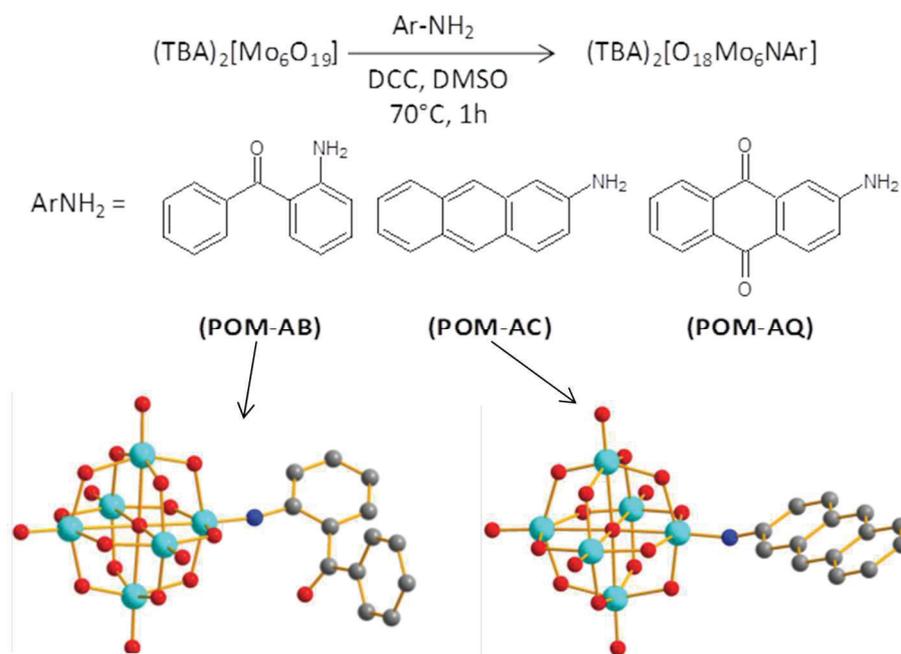
<sup>a</sup> Université Paris-Saclay, UVSQ, CNRS, Institut Lavoisier de Versailles, 45 avenue des Etats-Unis, 78000 Versailles.

<sup>b</sup> Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR-CNRS 7182, 2-8 rue Henri Dunant, 94320 Thiais.

Zeinab.el-hajj@uvsq.fr, <https://www.ilv.uvsq.fr/en>

**Keywords:** Polyoxometalates; organoimido derivatives; photopolymerization;

**Texte:** We present the synthesis and use of new hybrid polyoxometalates (POMs) as photoinitiating systems when associated to N-methyldiethanolamine (MDEA, an electron donor) for the free-radical photopolymerization of acrylate derivatives. Three original organoimido derivatives  $(\text{TBA})_2[\text{O}_{18}\text{Mo}_6(\text{NC}_6\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_5)]$  (**POM-AB**),  $(\text{TBA})_2[\text{O}_{18}\text{Mo}_6(\text{NC}_{14}\text{H}_9)]$  (**POM-AC**) and  $(\text{TBA})_2[\text{O}_{18}\text{Mo}_6(\text{NC}_{14}\text{H}_7\text{O}_2)]$  (**POM-AQ**) which consist on the covalent grafting of benzophenone, anthracene or anthraquinone moiety respectively on the POM platform have been synthesized and fully characterized. Notably, these compounds were optimally obtained in a very short reaction time (1h) in comparison to previously reported POM imido derivatives.<sup>1</sup> As expected, the strong electronic interactions between the hexamolybdate core and the organic part through Mo-N triple bond lead to a strong red shift of the absorption bands in the UV-Vis spectra along with higher  $\epsilon$  values compared to the organic precursors. As a consequence, these POM-based systems interestingly appear as efficient photoinitiators working under visible light irradiation.



**Figure:** Top: synthetic pathway of the organoimido POM derivatives (**POM-AB**, **POM-AC** and **POM-AQ**). Down: molecular structures of **POM-AB** (left) and **POM-AC** (right). TBA cations and H atoms were omitted for clarity. Turquoise spheres: Mo, red spheres: O, blue spheres: N, grey spheres: C.

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## Heteroleptic dirhodium(II) complexes with redox-active ferrocenyl ligands for redox-responsive catalysis

A. Labande,<sup>a</sup> I. Ruzhylo,<sup>a</sup> A. Sournia-Saquet,<sup>a</sup> A. Moreau,<sup>a</sup> T. Delord,<sup>a</sup> E. Manoury<sup>a</sup> et R. Poli,<sup>a,b</sup>

<sup>a</sup> LCC-CNRS, Université de Toulouse, CNRS, INPT, 205 route de Narbonne, 31077 Toulouse

<sup>b</sup> Institut Universitaire de France, 1, rue Descartes, 75231 Paris

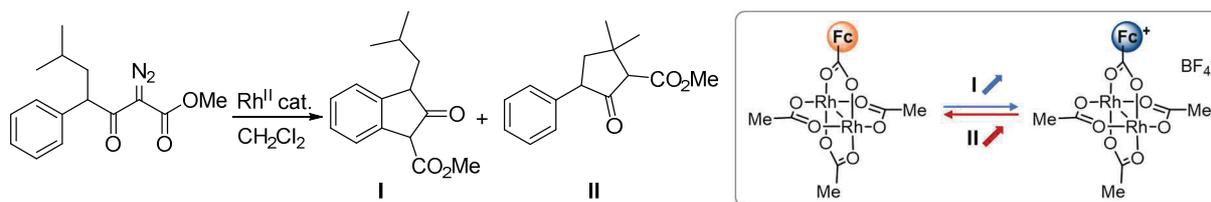
agnes.labande@lcc-toulouse.fr, <https://www.lcc-toulouse.fr>

**Keywords** : ferrocene; dirhodium; diazo compounds; oxidation; electrochemistry

Since the pioneering work of Wrighton,<sup>1</sup> redox-active ligands have been used to alter a catalyst reactivity (redox-switchable catalysis).<sup>2</sup> Most examples rely on ferrocene, the redox behaviour of which is well-known and which offers a wide range of possibilities for functionalization. Dirhodium(II) complexes bearing ferrocenyl ligands have been reported as early as 1982 and since then, various ferrocene-based ligands have been introduced.<sup>3</sup> However, surprisingly, the redox-active character of ferrocene has never been exploited in this chemistry.

We describe here the synthesis of several ferrocene-based carboxylic acids and of the corresponding heteroleptic [Rh<sub>2</sub>(OAc)<sub>3</sub>(L)] complexes, where L is the ferrocenyl-functionalised ligand. Their electrochemical properties have been investigated and a few selected dirhodium(II) complexes have been used in the catalysed intramolecular decomposition of a diazo substrate.

We showed that the oxidation of the ferrocenecarboxylate ligand has an effect on the chemoselectivity of the dirhodium-catalysed diazo decomposition, and thus that the electronic properties of a complex can be tuned without exchanging ligands.<sup>4</sup>



**Fig. 1** Rh(II)-catalysed decomposition of a diazo compound: effect of ferrocenyl ligand oxidation on the I:II ratio.

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# ORGANOLANTHANIDE COMPLEXES WITH LARGE AROMATIC LIGANDS

J. Piątkowski,<sup>a</sup> G. Danoun,<sup>a</sup> G. Nocton<sup>a</sup>

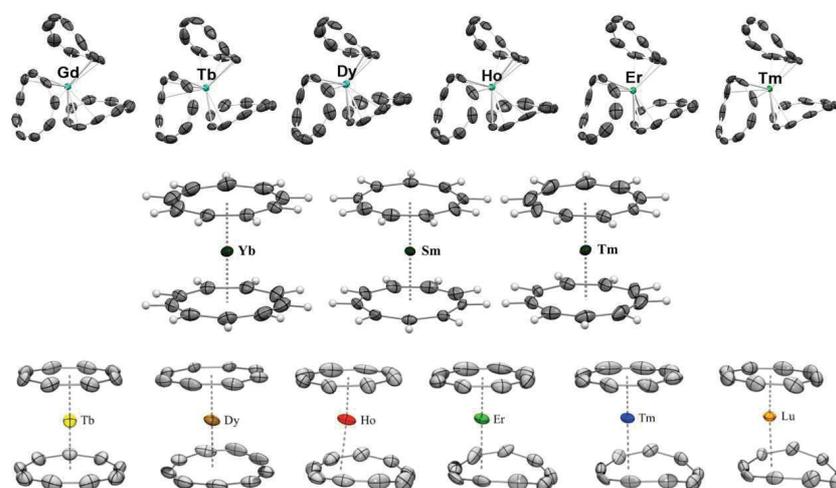
<sup>a</sup> *Laboratoire de Chimie Moléculaire (LCM), CNRS, Ecole Polytechnique, 91120, Palaiseau*  
 jakub.piatkowski@polytechnique.edu, <http://www.gregory.nocton.fr>

**Keywords:** organolanthanides; aromatic ligands; sandwich complexes; *f*-elements;

**Texte:** The organometallic chemistry of lanthanides has long been dominated by the use of the classical 5-membered monoanionic cyclopentadienyl (Cp) ligand and its derivatives.<sup>1</sup> Another major impetus in the organolanthanide chemistry was brought by the introduction of the larger and dianionic cyclooctatetraene (COT) ligand, which led to the synthesis and characterisation of numerous examples of lanthanide complexes.<sup>2</sup> With the exception of the COT ligand, organolanthanide complexes containing large aromatic ligands (7 or more atoms in the ring system) are relatively scarce.<sup>3</sup>

Over the past few years, we have been interested in the development of novel lanthanide complexes featuring large carbon-based ligands, especially the monoanionic 9-membered cyclononatetraenyl (Cnt) ligand (Figure 1).<sup>4</sup> Such ligands may confer promising magnetic properties to the corresponding Ln complexes,<sup>5-6</sup> as well as provide modular coordination modes.<sup>7</sup> For example, using the Cnt ligand, linear<sup>4</sup> and propeller-like<sup>8</sup> complexes were obtained using divalent and trivalent lanthanides, respectively (Figure 1).

Current research ongoing in our laboratory is directed to the design of novel organolanthanide complexes containing larger and more expanded aromatic ligands in order to tune their magnetic and structural properties.



**Fig. 1** Organolanthanide complexes containing large (8- and 9-membered) aromatic ligands developed by our group.

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## Temperature sensors based on europium polyoxometalate and mesoporous terbium metal–organic framework

C. Viravaux<sup>a</sup>, O. Oms<sup>a</sup>, A. Dolbecq<sup>a</sup>, E. Nassar<sup>a</sup>, L. Busson<sup>a</sup>, C. Mellot-Draznieks<sup>b</sup>, R. Dessapt<sup>c</sup>, H. Serier-Brault<sup>c</sup> and P. Mialane<sup>a</sup>.

<sup>a</sup> Université Paris-Saclay, UVSQ, CNRS, Institut Lavoisier de Versailles, 78000 Versailles.

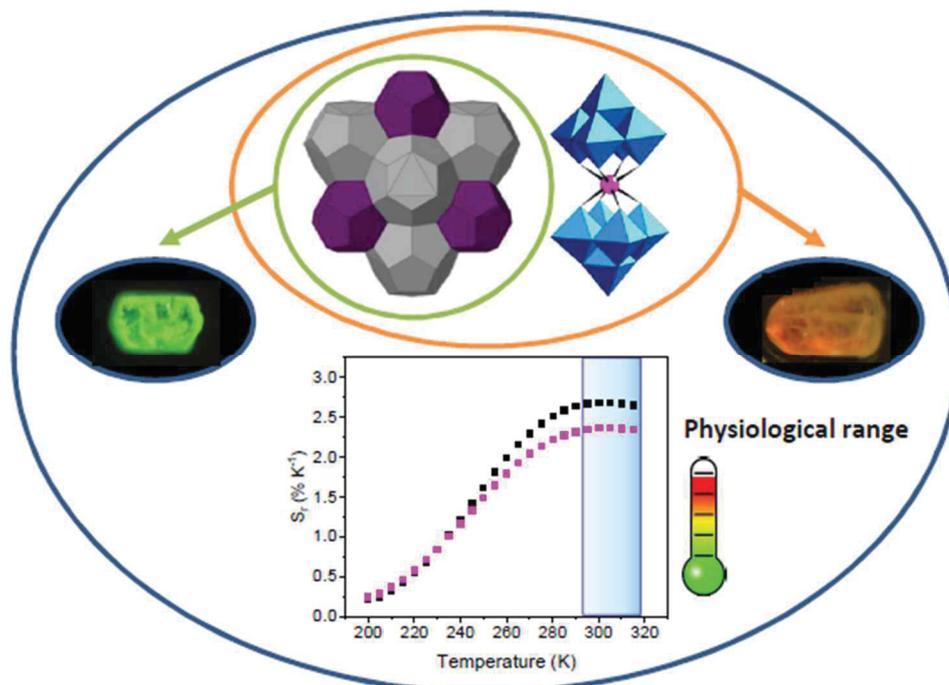
<sup>b</sup> Laboratoire de Chimie des Processus Biologiques, UMR CNRS 8229, Collège de France, Sorbonne Université, PSL Research University, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05.

<sup>c</sup> Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, IMN F-44000, Nantes.

[cedric.viravaux@uvsq.fr](mailto:cedric.viravaux@uvsq.fr), <https://www.ilv.uvsq.fr/en>

**Keywords:** Polyoxometalate; Metal-Organic-Framework; Biluminescence, Temperature sensor.

**Texte:** We report the first example of ratiometric luminescent thermometers based on lanthanide molecular species encapsulated in a lanthanide metal–organic framework (MOF). In EuW<sub>10</sub>@Tb-TATB, the [EuW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> polyoxometalate (POM) is incorporated into the cavities of the mesoporous terbium MOF Tb-TATB with two different POM loadings (9.1 and 19.5 wt%). Eu<sup>3+</sup> and Tb<sup>3+</sup> ions of the POM and MOF, respectively, act as emitters. Noticeably, optical measurements evidence efficient Tb<sup>3+</sup>-to-Eu<sup>3+</sup> energy transfer, suggesting that the EuW<sub>10</sub> units are close to terbium centers. These observations are supported by computational investigations whereby a favored localisation of the POM in the MOF's pores evidences hydrogen bonding between terminal oxygen atoms of the POM and Tb-coordinated water molecules. Importantly, the reported materials act as a temperature sensor in the physiological domain, exhibiting high relative thermal sensitivities of 2.68% K<sup>-1</sup> and 2.37% K<sup>-1</sup> at 300 K for the 9.1 POM wt% and 19.5 POM wt% composites, respectively, with a thermal uncertainty of 0.09 K.<sup>1</sup>



**Fig. 1** Representation of the two components of the EuW<sub>10</sub>@Tb-TATB composites, images of crystals of Tb-TATB and EuW<sub>10</sub>@Tb-TATB under 365 nm irradiation and the relative thermal sensitivity of the two composites.

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# Unprecedented Lactide-Lactone Chain Shuttling Copolymerization Mediated by Aluminum-based complexes

Fanny Bonnet,<sup>a\*</sup> Julie Meimoun,<sup>b</sup> Choltirosn Sutapin,<sup>c</sup> Gregory Stoclet,<sup>a</sup> Audrey Favrelle-Huret,<sup>b</sup> Pascal Roussel,<sup>b</sup> Marc Bria,<sup>d</sup> Suwabun Chirachanchai,<sup>c</sup> Philippe Zinck<sup>b\*</sup>

<sup>a</sup> *Unité Matériaux et Transformations (UMET), UMR 8207, Univ. Lille, CNRS, INRAE, Centrale Lille F-59650, Villeneuve d'Ascq, France*

<sup>b</sup> *Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181, Univ. Lille, CNRS, Centrale Lille, Univ. Artois, F-59650, Villeneuve d'Ascq, France*

<sup>c</sup> *Bioresources Advanced Materials Research Unit (B2A) The Petroleum and Petrochemical College, Chulalongkorn University Pathumwan, Bangkok, 10330, Thailand*

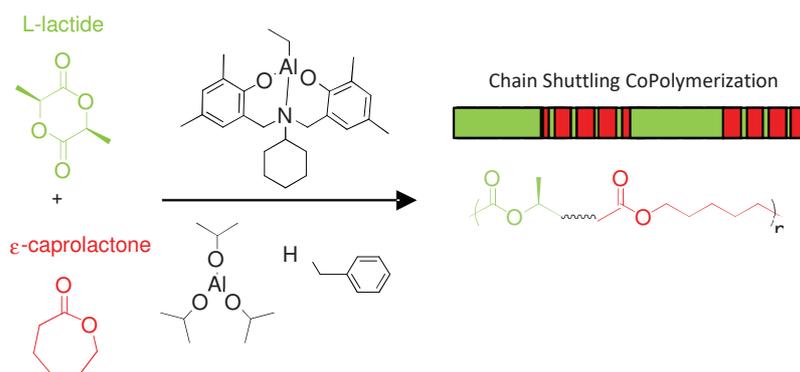
<sup>d</sup> *Plateforme RMN, Univ. Lille, CNRS, Centrale Lille, Univ. Artois, F-59650, Villeneuve d'Ascq, France*

fanny.bonnet@univ-lille.fr, <http://umet.univ-lille1.fr/>

**Keywords** : Chain shuttling copolymerization, Aluminum complex, Polylactide, Block copolymers

Chain shuttling copolymerization (CSP), is a powerful tool allowing the access to multiblock / segmented copolymers with original microstructures in a one-pot one-step route.<sup>1</sup> In CSP, initially developed for ethylene / 1-alkene systems,<sup>1</sup> the growing macromolecular chain is allowed to “shuttle” by transmetalation via an organometallic chain transfer agent (CTA) between two catalysts presenting a difference in comonomers reactivity ratios, and thus leading to statistical copolymeric blocks of different composition. If chain shuttling homopolymerization systems, where only one monomer is involved, have been well explored,<sup>2</sup> it appears that since the seminal work on ethylene/1-alkene comonomers, the synthesis of original multiblock microstructures by chain shuttling copolymerization was extended to only one other comonomers combination, *i.e.* styrene / conjugated diene, by rare earth based catalysts.<sup>3</sup>

In the present work, the unprecedented CSP of two polar monomers, L-lactide and  $\epsilon$ -caprolactone, has been achieved by Ring Opening Polymerization (ROP) monitored by two aluminum catalysts presenting different selectivities and benzyl alcohol as the chain transfer agent. A newly synthesized aminobisphenolate-supported aluminum complex affords the formation of lactone rich poly(L-lactide-co-lactone) statistical copolymeric blocks, while  $\text{Al}(\text{O}i\text{Pr})_3$  produces semi-crystalline poly(L-lactide) rich blocks.<sup>4</sup>



**Fig. 1** Lactide-lactone chain shuttling copolymerization involving two aluminum-based catalysts and a chain transfer agent (CTA, BnOH in the present work)

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# Synthesis of Amidinium Dithiocarboxylate Zwitterions Derived from Caffeine and Theophylline and their Use as Ligands for Transition Metal Complexes

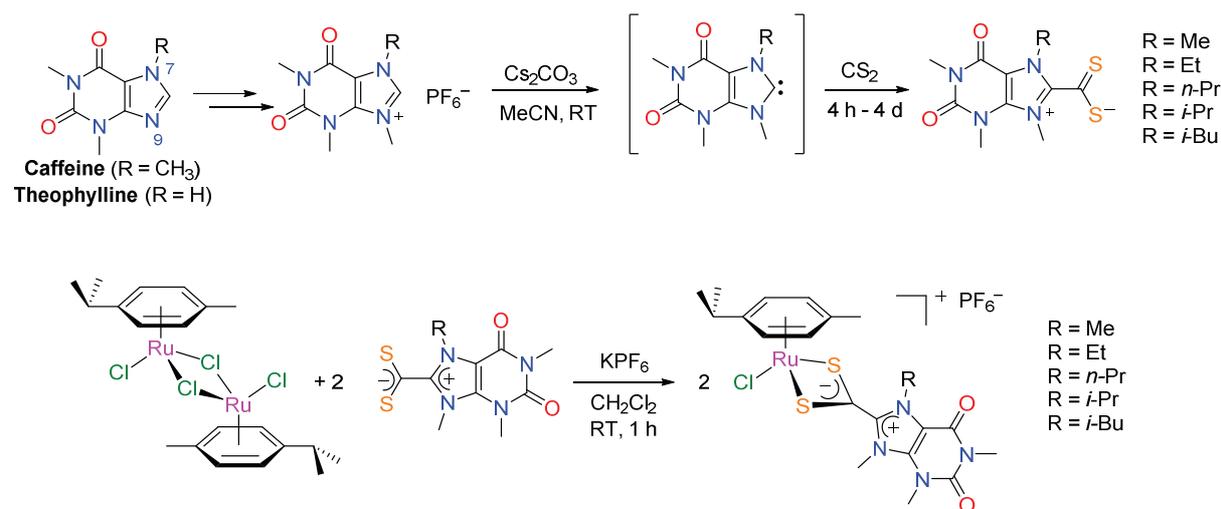
François MAZARS,<sup>a</sup> Lionel DELAUDE <sup>a</sup>

<sup>a</sup> Laboratory of Organometallic Chemistry and Homogeneous Catalysis,  
University of Liege, Allée du six août 13, 4000 Liege, Belgium  
f.mazars@doct.uliege.be

**Keywords** : Dithiocarboxylate, Zwitterion, Ruthenium-Arene Complexes

Herein we disclose simple and efficient experimental protocols for the synthesis of new amidinium-2-dithiocarboxylate betaines derived from caffeine and theophylline via the intermediacy of N-heterocyclic carbenes (NHCs). The NHC·CS<sub>2</sub> zwitterions obtained will serve as ancillary ligands to prepare a wide range of transition metal complexes, whose biological activities and catalytic properties will be evaluated. Preliminary results achieved for the synthesis of ruthenium complexes are described.

Caffeine and theophylline are two substrates of choice for generating new ligand systems, thanks to their wide availability from natural sources, low cost of extraction, and ability to form different types of carbenes. However, caffeine is an extremely poor nucleophile and we were only able to methylate its N9 position using trimethyloxonium tetrafluoroborate under harsh conditions. Recourse to other alkylating agents remained largely unsuccessful. To circumvent this difficulty, we reasoned that longer alkyl chains should be first introduced onto theophylline, which is more reactive toward nucleophilic substitution than caffeine, followed by a methylation of the intermediate N7 monoalkyl derivative. Indeed, this alternate strategy allowed us to synthesize a set of 1,3,9-trimethyl-7-alkylxanthinium salts with various chain lengths in moderate to good yields. We then successfully trapped the free carbene generated *in situ* from these imidazolium salts with carbon disulfide to form the corresponding NHC·CS<sub>2</sub> zwitterions. The cleavage of the [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> dimer with 2 equivalents of the NHC·CS<sub>2</sub> betaines obtained afforded monometallic ruthenium-arene complexes with the generic formula [RuCl(S<sub>2</sub>C·NHC)(*p*-cymene)]PF<sub>6</sub>. We also used 6 equivalents of the dithiocarboxylate ligands to prepare dicationic homoleptic [Ru(S<sub>2</sub>C·NHC)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> complexes.



**Fig. 1** Synthesis and complexation of dithiocarboxylates zwitterions derived from xanthines

# Crystalline structure of UiO-like MOF compounds bearing thorium with azobenzene dicarboxylate linker

D. Andriotou<sup>1</sup>, S. Duval<sup>1</sup>, C. Volkringer<sup>1</sup>, C. Mellot-Draznieks<sup>2</sup> and T. Loiseau<sup>1</sup>

<sup>1</sup>Unit of Catalysis and Solid State Chemistry (UCCS)-UMR CNRS 8181, Université de Lille, Cité Scientifique, 59650, Villeneuve d'Ascq, France

<sup>2</sup>Laboratory of Chemistry of Biological Processes, UMR CNRS 8229, Collège de France, Université Pierre et Marie Curie, PSL Research University, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05, France

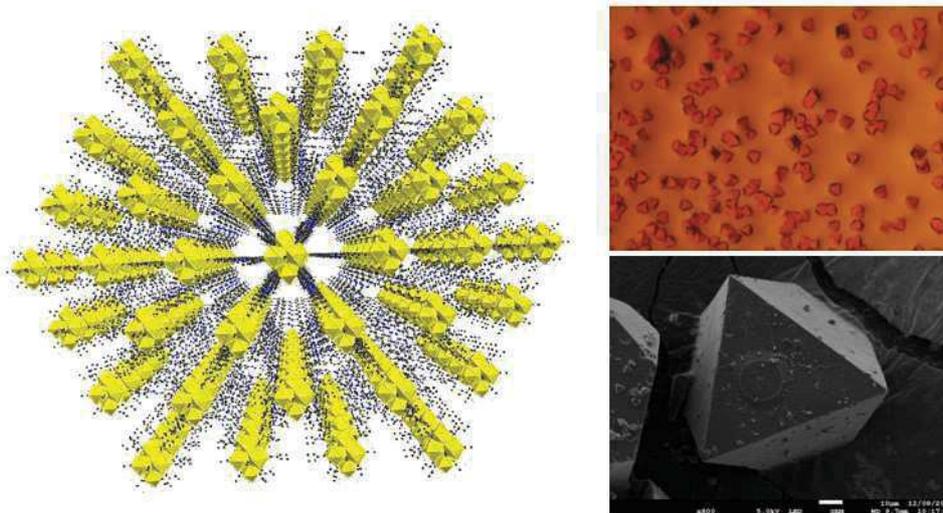
despoina.andriotou@univ-lille.fr

**Keywords:** metal-organic frameworks, thorium, azobenzene, BET surface area, gas sorption, modulators

Herein, we report the synthesis and the X-ray diffraction analysis of a porous UiO-type thorium-based Metal-Organic Framework (MOF) as  $\text{Th}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_6(\text{azbdc})_6 \cdot \text{DMF}$ . It is constructed from the hexanuclear secondary building unit (SBU) of  $\{\text{Th}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_6\}$  type, assembled in a 3D cubic network with the ligand 4,4'-azobenedicarboxylate (noted *azbdc*<sup>2-</sup>), which has been previously reported with the zirconium metallic center<sup>1</sup>. The crystal growth during the solvothermal synthesis was monitored by the use of a variety of different monocarboxylic acids as modulators (such as 2-naphtoïc acid and formic acid).

Full characterization study has been conducted for the different modulators, to optimize the BET surface area and the thermal stability of the framework. Indeed, by using a smaller modulator such as formic acid instead of the bulkier 2-naphtoïc acid, we obtain a BET surface area up to 1195 m<sup>2</sup>/g (from N<sub>2</sub> sorption at 77K) for the as-synthesized Th-UiO-azbdc. Moreover, different gas uptake performances have been evaluated for Kr, Xe, CH<sub>4</sub> and CO<sub>2</sub> adsorption at both 273K and 293K, with values of 9.3-7.1, 35.9-23.6, 7.7-6.1 et 24.9-11.7 cm<sup>3</sup>/g, respectively.

Finally, the accurate location of the backbones of the *azbdc*<sup>2-</sup> linker (except the carboxylate arms) was not possible from the single-crystal XRD analyzes, due to the occurrence of large statistical disorder. In order to get a complete view of the structure and circumvent the positional disorder of the linkers resulting from the diffraction analysis, we used dispersion-corrected density functional theory (DFT) level calculations to perform geometry optimizations of the periodic crystal structure and propose a precise localization and orientation of the *azbdc*<sup>2-</sup> linkers.



**Fig. 1** Structural, optical and scanning electron microscopy images of the Th-UiO-azbdc.

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# Merging helicenes and N-heterocyclic carbenes in enantioselective gold catalysis

Vincent César,<sup>a</sup> Lenka Pallova,<sup>a</sup> Etienne S. Gauthier,<sup>a</sup> Marion Jean,<sup>c</sup> Laura Abella,<sup>d</sup> Cécile Barthes,<sup>a</sup> Nicolas Vanthuyne,<sup>d</sup> Jochen Autschbach,<sup>c</sup> Jeanne Crassous,<sup>b</sup> Stéphanie Bastin<sup>a</sup>

<sup>a</sup> LCC-CNRS, Université de Toulouse, Toulouse, France

<sup>b</sup> ISCR, Université de Rennes 1, Rennes, France

<sup>c</sup> Ism2, Université Aix-Marseille, Marseille, France

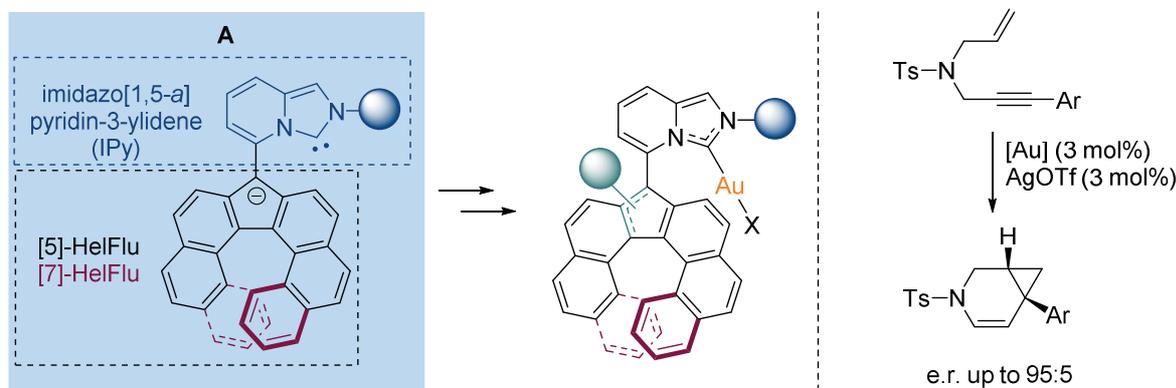
<sup>d</sup> University at Buffalo, Buffalo, NY, USA

vincent.cesar@lcc-toulouse.fr, <https://www.lcc-toulouse.fr/>

**Keywords** : Helicenes, Carbenes, Catalysis, Chirality, Gold, heterocycles

Over the last years, the combination of N-Heterocyclic Carbenes (NHCs) and helicenic moieties in ligand structures has gained great attention with significant developments mainly focused on chiral helicenic NHC-complexes with intriguing emission properties.<sup>[1]</sup> Conversely, the implementation of chiral helicenic NHC-complexes in asymmetric catalysis is still in its infancy with only two examples reported up to now.<sup>[2]</sup>

In this communication, we will present the new helicenic NHC **A**, in which the fluorenyl-derived [5] and [7]-HelFlu helicenes are grafted on the IPy core. An improved synthetic access toward the [5]- and [7]-HelFlu helicenes,<sup>[3]</sup> their coupling with the imidazopyridinium core by a S<sub>N</sub>Ar-type reaction, as well as the generation and coordination chemistry of NHC **A** and its derivatives will be described. The activity of the prepared gold(I) complexes in enantioselective gold-catalyzed reaction will be also presented.<sup>[4]</sup>



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## Microwave Synthesis of MOFs on Textiles for the Capture and Degradation of Chemical Warfare Agent Simulant

N. Couzon<sup>a</sup>, M. Ferreira<sup>b</sup>, A. El-Arachi<sup>b</sup>, C. Campagne<sup>b</sup>, R-M. Sauvage<sup>c</sup>, T. Loiseau<sup>a</sup>, C. Volkringer<sup>a</sup>

<sup>a</sup> Univ. Lille, CNRS, Centrale Lille, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France ; <sup>b</sup> GEMTEX–Laboratoire de Génie et Matériaux Textiles, ENSAIT, Univ. Lille, F-59000 Lille, France; <sup>c</sup> DGA-AID, F-75015 Paris

nelly.couzon@centralelille.fr/ christophe.volkringer@centralelille.fr

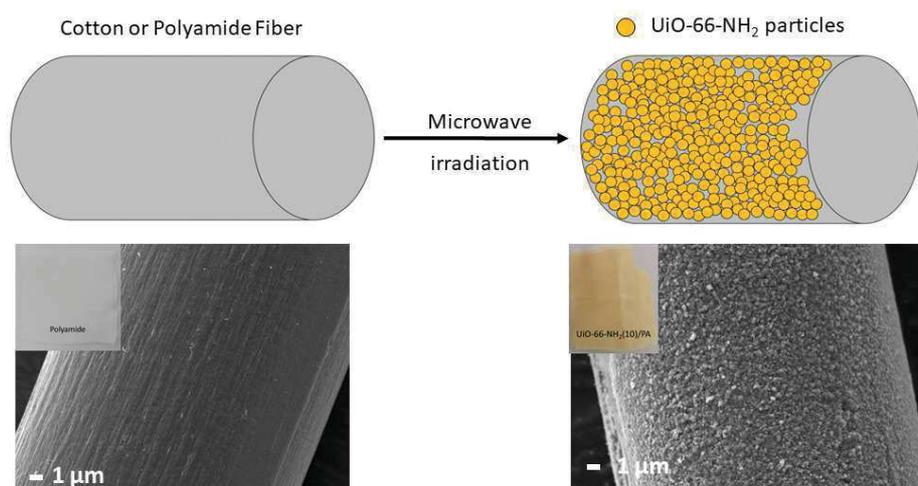
**Keywords:** Metal-Organic Framework (MOF); Microwave-assisted synthesis; textiles; DMNP degradation

### Abstract:

Due to the CBRN (Chemical, Biological, Radiological and Nuclear) threats, the development of efficient personal protective equipment (PPE) has been highly investigated. Recently, Metal-Organic Framework (MOF), a crystalline and highly porous hybrid material family, have appeared as a new promising candidate for the adsorption and/or degradation of chemical threats, like chemical warfare agents (CWAs).<sup>1</sup>

In this study, we present an innovative synthesis method of MOF-textile composite by microwave irradiation, which allows a direct anchoring of the MOFs on fibers (Fig. 1). Research has been focused on two Zr-based MOFs, UiO-66 and UiO-66-NH<sub>2</sub>, which are known for their efficiency in CWA detoxification. To enhance the amount of MOF deposited and therefore the detoxification capacity, multilayers of MOFs have been synthesized. Due to the importance of mechanical strength for PPE, normed abrasion tests have been performed. Stable composites were obtained with polyamide (PA) fibers, while cotton fibers were fragilized by the microwave synthesis.

The protective efficiency of the MOF/textile composite have then been tested against a chemical threat, i.e dimethyl n-nitrophenylphosphate DMNP, a common CWA simulant. The best composite for DMNP degradation was found for a 10 layered UiO-66-NH<sub>2</sub>/polyamide composite, showing a short half-life, i.e. the time to detoxify 50 % of DMNP, of 30 min.<sup>2</sup>



**Fig. 1** Schema and SEM images of polyamide fiber functionalized by UiO-66-NH<sub>2</sub> particles with microwave-assisted synthesis.

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# MECHANISTIC STUDY OF COPPER-CATALYZED REVERSIBLE DECARBOXYLATION PROCESS

## TITRE (Arial, 14 pts, gras; 2 lignes maximum; interligne simple)

K. Phung,<sup>a</sup> J.-C. Berthet,<sup>a</sup> et T. Cantat,<sup>a</sup>

<sup>a</sup> LCMCE, IRAMIS, NIMBE, CEA, CNRS, Université Paris-Saclay, 91191 Gif-sur-Yvette, France  
[kieu.phung@cea.fr](mailto:kieu.phung@cea.fr), <https://iramis.cea.fr/Pisp/thibault.cantat/>

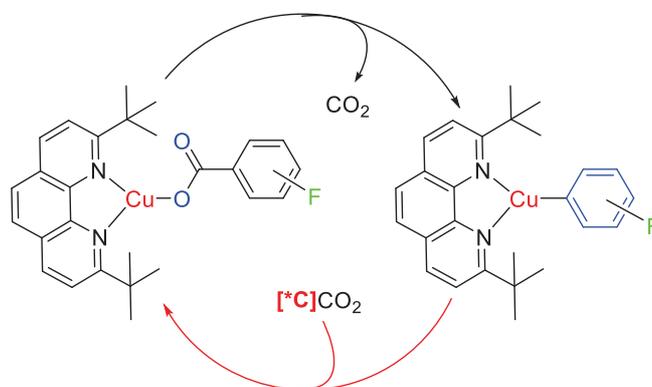
**Keywords** : Coordination chemistry; Copper complexes; Decarboxylation/carboxylation catalysis.

Copper-catalyzed decarboxylation process of aromatic carboxylic acids has been intensively studied thanks to its efficiency in the formation of C-C or C-heteroatom bonds.<sup>1</sup> However, limited substrate scopes and forcing reaction conditions remains as drawbacks.<sup>2,3</sup> Therefore, a mechanistic understanding of these processes is of interest to facilitate these complex systems.

One proposition to exploit these systems is to track the process by dynamic isotope exchange. This reversible decarboxylation reaction has been successfully proved, in which <sup>14</sup>CO<sub>2</sub> (or <sup>13</sup>CO<sub>2</sub>) was transferred to a series of aryl carboxylic salts using copper as catalyst.<sup>4</sup>

To carried on from this work, and because nitrogen ligand are helpful for this transformation, the aim is to isolate potential copper(I) intermediates with the choice of phenanthroline (phen) as ligand. Once different copper(I) species are isolated and characterized, the goal is to investigate their reactivity toward decarboxylation/carboxylation processes via multiple analysis methods, for instance, NMR spectroscopy, cyclic voltammetry and DFT calculation.

In order to enhance copper(I) aryl complexes stability and to avoid common redistribution of the ligand,<sup>5,6</sup> we focus on the bulky 2,9-ditertbutyl-1,10-phenanthroline ligand (dtbp),<sup>7</sup> which was applied for the synthesis of aryl carboxylated and aryl copper(I) complexes.



**Fig. 1** Copper-catalyzed dynamic isotope exchange of CO<sub>2</sub>

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# Synthesis of hydroboranes from chloroboranes hydrogenolysis and one-pot applications

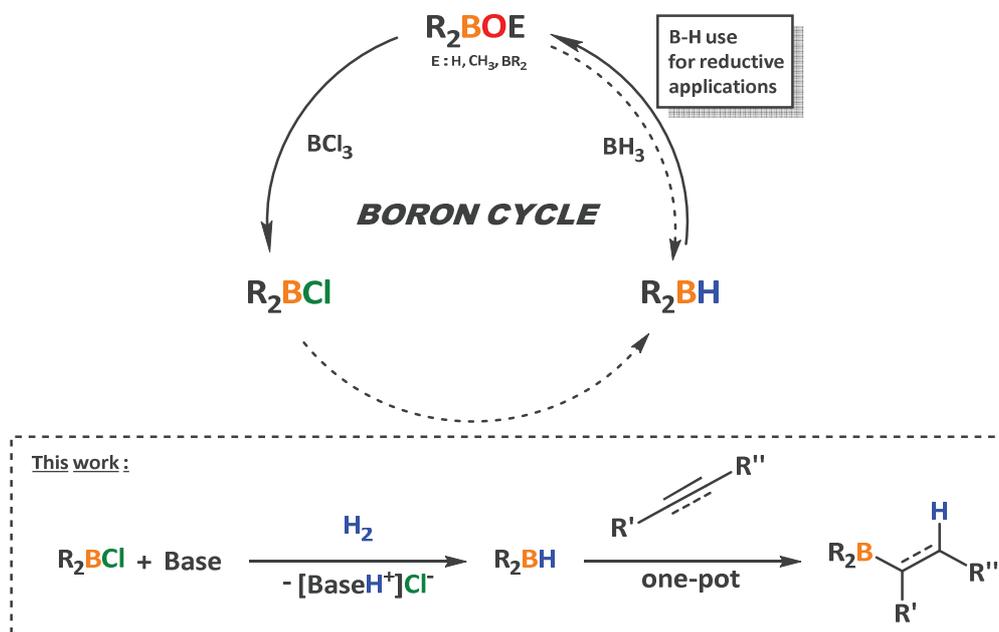
G. Zwart, A. Mifleur, G. Durin, J-C. Berthet, T. Cantat

Laboratoire de Chimie Moléculaire et de Catalyse pour l'Énergie – Université Paris-Saclay, CEA, CNRS, NIMBE  
 guilhem.zwart@cea.fr, <https://iramis.cea.fr/Pisp/thibault.cantat/>

**Keywords** : boranes ; chloroboranes ; hydrogenolysis

## Text:

Human energetic paradigm currently implies getting low oxidation state carbon (fossil oil) to upper states (as CO<sub>2</sub>). To move from this linear system to a more sustainable one, renewable carbon sources such as biomass or polymer wastes are good candidates but are often highly oxidized. Therefore, to valorize such substrate, versatile reductants and related methodologies are required. Hydroboranes present suitable electro-redox potential for the carbon-oxygen bonds reduction. A major drawback is the synthesis of such reductants, highly energy consuming. The hydroboranes are synthesized from BH<sub>3</sub>,<sup>1</sup> and end as oxygenated wastes after use. Activation of small molecules such as hydrogen is well-known with boron derivative in the Frustrated Lewis Pair (FLP) chemistry<sup>2</sup>. Herein we report the first example of H<sub>2</sub> activation and followed by hydrogenolysis of the B-chloroborane bond to form hydroborane derivatives in quantitative yields. We also found that in our method the chloroborane can act as surrogate for hydroborane given our hydrogenolysis conditions are compatible with hydroboration conditions, allowing domino reactions without hydroborane isolation. Thus, this extends the possible applications of chloroboranes in synthesis. It also paves the way for hydroboranes synthesis from other B-X compounds.



**Fig. 1** : Hydrogenolysis of chloroboranes in boranes with an organic base, applications and context

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