Journées de Chimie de Coordination – 2019

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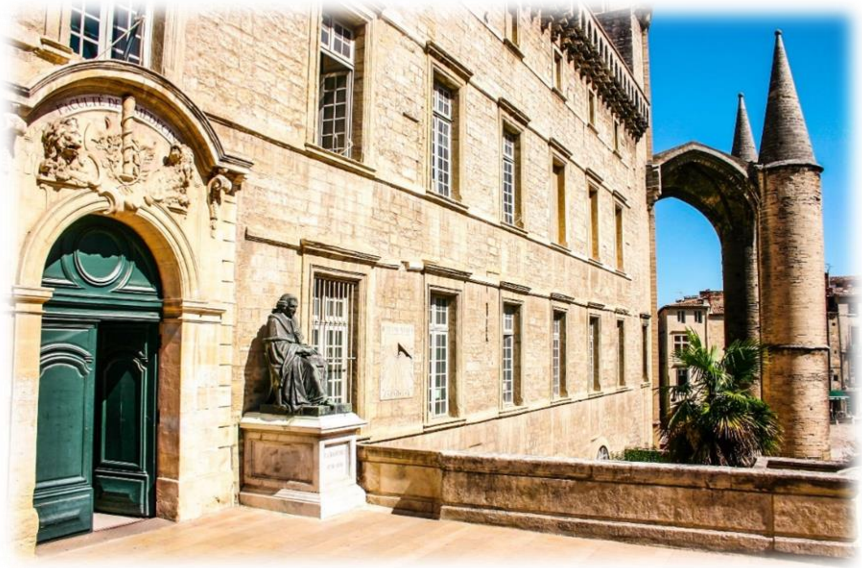
du 31 janvier au 1 février 2019 à Montpellier (France)



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Recueil des résumés

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Le Mot de la Societe Chimique de France

Chers Amis, chers Collègues,

Voici venu le tour de Montpellier d'accueillir le rendez-vous annuel des Journées de Chimie de Coordination et le bureau de la Division adresse ses plus vifs remerciements à l'équipe organisatrice représentant les quatre grands instituts de chimie de Montpellier, l'Institut Charles Gerhardt, l'Institut des Biomolécules Max Mousseron, l'Institut Européen des Membranes et l'Institut de Chimie Séparative de Marcoule, et tout particulièrement à Armelle Ouali et Sébastien Richeter.

Il est à parier que l'édition 2019 sera de nouveau très enrichissante, avec 6 conférences plénières illustrant toute la diversité de notre discipline et 18 communications orales attestant de sa vitalité. Comme il est de coutume, le prix 2018 de la DCC, prix senior, sera officiellement remis à Jean-François Nierengarten pour ses contributions majeures à la chimie des fullerènes, des complexes cuivreux luminescents et à la chimie supramoléculaire, entre autres. Nous annoncerons aussi le lauréat du premier prix de thèse de la DCC.

C'est aussi à l'occasion de ces JCC que se mettra en place le bureau nouvellement élu de notre division. C'est ainsi le moment pour le bureau sortant de faire un bilan des trois années écoulées. Trois années riches d'évènements marquants, comme les 40 ans de la Division (voir article publié sur l'Actualité Chimique N° 424 de décembre 2017) et le Prix Nobel de Jean-Pierre Sauvage. Une nouvelle initiative de notre bureau a été le lancement de la Newsletter bisannuelle de la Division. Elle a reçu un accueil très favorable et a peu à peu trouvé sa place comme un nouvel outil de diffusion des informations relatives à notre activité de chimistes de coordination. Nous avons poursuivi le soutien aux plus jeunes chercheurs pour leur participation aux congrès internationaux et soutenu dans la mesure de nos moyens l'organisation de manifestations locales ou nationales. Il nous faut poursuivre les efforts entrepris pour entretenir les interfaces avec les autres divisions de la SCF, comme nous avons pu le faire lors d'éditions précédentes des JCC ou lors du congrès SCF 18, mais aussi vers les divisions similaires à la DCC en Europe pour accroître encore notre visibilité.

Nous vous souhaitons une très bonne année et de très bonnes Journées à Montpellier, avec de nombreux échanges scientifiques dans une atmosphère conviviale !

Le bureau de la Division de Chimie de Coordination de la SCF :
Ally Aukauloo, Yves Canac, Yves Le Mest, Lorraine Christ,
Anna Proust et Rinaldo Poli

Le Mot du Comité du Comité d'Organisation

Bienvenue aux Journées de Chimie de Coordination 2019

Chères participantes, chers participants,

C'est avec beaucoup de plaisir que nous vous accueillons à Montpellier pour les Journées de Chimie de Coordination 2019 sous l'égide de la Division de Chimie de Coordination de la Société Chimique de France. Comme chaque année, cette manifestation constitue une occasion privilégiée de rencontres dans un cadre convivial permettant de faire le point sur les avancées en chimie de coordination et ses applications, d'échanger des idées et de nouer de futures collaborations.

Nous tenons à exprimer notre plus sincère reconnaissance à l'ensemble des institutions publiques et des partenaires privés qui ont soutenu ces journées et dont les logos figurent sur la page suivante. Enfin, nous vous remercions pour votre venue qui illustre le dynamisme et la vitalité de notre communauté de chimistes de coordination !

Nous vous souhaitons de passer un colloque enrichissant et un agréable séjour à Montpellier.

Le Comité d'Organisation

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Le Comité d'Organisation des Journées de Chimie de Coordination 2019 adresse ses plus sincères remerciements aux entreprises, organismes et tutelles qui ont soutenu cette manifestation scientifique.

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Programme des Journées de Chimie de Coordination 2019

Montpellier, 31 janvier & 1er février 2019

Jeudi 31 janvier 2019		
12h00-13h00	Accueil des participants & café	
13h00-13h10	Ouverture	
13h10-13h55	CP1	Myrtil Kahn
13h55-14h15	CO1	Elodie Rousset
14h15-14h35	CO2	Maya Guillaumont
14h35-14h55	CO3	Guillaume Izzet
14h55-15h15	CO4	Damien Brunel
15h15-15h30	Communications Sponsors	
15h30-16h00	Pause Café	
16h00-16h45	CP2	Eduardo Peris
16h45-17h05	CO5	Jordan Donat
17h05-17h25	CO6	Franck Ulm
17h25-17h45	CO7	Damien Bechu
17h45-18h05	CO8	Rinaldo Poli (président DCC)
18h05-18h35	Andrew Shore (Editeur RSC)	
18h35-22h00	Session Posters & Buffet Dînatoire	

Vendredi 1er février 2019		
8h00-8h45	CP3	Corine Mathonière
8h45-9h05	CO9	Ding Wang
9h05-9h25	CO10	Racha Abed Ali Abdine
9h25-9h45	CO11	Stéphanie Bastin
9h45-10h15	Pause Café	
10h15-11h00	CP4	Clotilde Policar
11h00-11h20	CO12	Emmanouil Giannoudis
11h20-11h40	CO13	Anton Ivanov
11h40-12h00	CO14	Sébastien Goeb
12h00-13h30	Déjeuner Buffet	
13h30-14h15	CP5	Jean-François Nierengarten (Prix DCC 2018)
14h15-14h35	CO15	Alexandra Fateeva
14h35-14h55	CO16	Agnès Labande
14h55-15h25	Pause Café	
15h25-16h10	CP6	Abderrahmane Amgoune
16h10-16h30	CO17	Miguel Monge
16h30-16h50	CO18	Orestes Rivada Wheelaghan
16h50-17h00	Remise des Prix & Clôture	

Programme des Journées de Chimie de Coordination 2019

Montpellier, 31 janvier & 1er février 2019

Jeudi, 31 Janvier 2019

12:00-13:00 **Accueil + Café**

13:00-13:10 **Ouverture**

13:10-13:55 **CP1. Synthesis of metal oxide nanoparticles by organometallic approach: from molecule to devices**
Myrtil L. Kahn

13:55-14:15 **CO1. On the use of ruthenium(II) polypyridyle building blocks in linear and non-linear optical systems**
Elodie Rousset, Sylviane Chevreux, Garry Hanan, Valerie Marvaud, Gilles Lemercier

14:15-14:35 **CO2. Theoretical study of Reduction Routes of $MX(PPh_3)_3$ in complex environment toward synthesis of Cobalt and Nickel Nanocrystals**
Maya Guillaumont, Hélène Gérard, Stéphanie Halbert, Marc Petit, Christophe Petit

14:35-14:55 **CO3. Hierarchichal self-assembly of polyoxometalate-based hybrids driven by metal coordination and electrostatic interactions**
Guillaume Izzet, Madeleine Piot, Raphaël Salles, Anna Proust

14:55-15:15 **CO4. New way to rectify current thanks to ferrocenyl triazole derivatives**
Damien Brunel, Clément Reynaud, David Duché, Ludovic Escoubas, Didier Gigmes, Frédéric Dumur

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15:15-15:30 **Communications Sponsors**

15:30-16:00 **Pause café**

16:00-16:45 **CP2. Polyaromatic-adorned N-Heterocyclic Carbenes. From Homogeneous Catalysis to Host-guest chemistry studies**
Eduardo Peris

16:45-17:05 **CO5. Binuclear μ-nitrido iron complexes for nitrene transfer in catalysis**
Jordan Donat, Jacques Pécaut, Jean-Marc Latour

17:05-17:25 **CO6. Synthesis and application in aldehyde hydrosilylation of nickel(II) complexes bearing hemilabile thioether-functionalised NHC ligands**
Franck Ulm, Amalia I. Pobaldor-Bahamonde, Michael J. Chetcuti, Thierry Achard, Vincent Ritleng

17:25-17:45 **CO7. Interdigitation for the elaboration of conducting MOFs**
Damien Bechu, Lilia Xie, Stéphane Baudron, Sylvie Choua, Mircea Dinca, Mir Wais Hosseini

17:45-18:05 **CO8. Nouveaux complexes fluoroalkyles [Mn(RF)(CO)$_5$] : force homolytique, génération de radicaux fluoroalkyles et α-F élimination**
Roberto Morales-Cerrada, Christophe Fliedel, Jean-Claude Daran, Florence Gayet, Vincent Ladmiral, Bruno Améduri, Rinaldo Poli

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18:05-18:35 **Andrew Shore – Editeur RSC**

Session Posters
18:35-22:00 **+**
Buffet Dînatoire

Vendredi, 1er Février 2019

08:00-08:45 **CP3. Cyanido-bridged Fe/Co pairs: how to make them and how to study the switching mechanism**
Corine Mathonière

08:45-09:05 **CO9. Synthesis and Characterizations of an Original Heterobimetallic Nickel Complex with Divalent Organolanthanides**
Ding Wang, Violaine Goudy, Jules Moutet, Marie Cordier, Grégory Nocton

09:05-09:25 **CO10. Regio- and Stereoselective Copper-Catalyzed Allylation of 1,3-dicarbonyl compounds with Terminal Allenes**
Racha Abed Ali Abdine, Rémi Blieck, Marc Taillefer, Florian Monnier

09:25-09:45 **CO11. Functionalized imidazo[1,5-a]pyridin-3-ylidene (IPy) ligands: Synthesis, coordination chemistry and catalysis**
Stéphanie Bastin, Idir Benaissa, Mathieu Huynh, Marie-Emilie Morantin, Yue Tang, Noël Lugan, Véronique Michelet and Vincent César

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09:45-10:15 **Pause café**

10:15-11:00 **CP4. Metal complexes in biological environments: a new frontier in inorganic chemistry**
Clotilde Policar

11:00-11:20 **CO12. A new RuCo dyad for dye-sensitized hydrogen-evolving photocathode applications**
Emmanouil Giannoudis, N. Queyriaux, V. Artero, Murielle Chavarot-Kerlidou

11:20-11:40 **CO13. Supramolecular host-guest recognition of Re6 clusters with cyclodextrins: size-matching and chaotropic effect**
Anton A. Ivanov, Clément Falaise, Mohamed Haouas, Yuri V. Mironov, Emmanuel Cadot

11:40-12:00 **CO14. Cages auto-assemblées riches en électrons : contrôle redox de transformations supramoléculaires**
Sébastien Goeb, Vincent Croué, György Szalóki, Serhii Krykun, Marc Sallé

12:00-13:30 **Déjeuner Buffet**

13:30-14:15 **CP5. From photoactive fullerene-donor conjugates to luminescent copper(I) complexes**
Jean-François Nierengarten

14:15-14:35 **CO15. Exploring versatile catalytic activity of stable porphyrin based MOFs**
Alexandra Fateeva, Jean-Bernard Tommasino, Gia Co Quan, Brian, Abeykoon, Thomas Devic, Alexander Sorokin, Aude Demessence, Fréderic Maillard

14:35-14:55 **CO16. Hydrosoluble Polymeric Nanoreactors Containing Rh(I)-NHC Complexes for Biphasic Catalysis**
Sasaline Salomon Sambou, Audrey Allandrieu, Eric Manoury, Rinaldo Poli, Agnès Labande, Florence Gayet

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14:55-15:25 **Pause café**

15:25-16:10 **CP6. Ligand design in Au(I)/Au(III) chemistry: From fundamental organometallic studies to the development of new gold catalysis**
Abderrahmane Amgoune

16:10-16:30 **CO17. Synthesis of complex or hybrid plasmonic nanostructures from organometallic precursors through ligand- or surface-controlled protocols**
Miguel Monge, Julian Crespo, Marta Jiménez-Salcedo, José M. López-de-Luzuriaga, M. Elena Olmos, Javier Quintana, María Rodríguez-Castillo, M. Teresa Tena

16:30-16:50 **CO18. Multimetallic CuI-PdII Linear Chain Complexes. Molecular Models for Sonogashira Coupling Reactions**
Orestes Rivada-Wheelaghan, Julia K. Khusnutdinova

16:50:17:00 **Remise des Prix & Clôture**

Conférences
Plénières

Synthesis of metal oxide nanoparticles by organometallic approach: from molecule to devices

Myrtil L. Kahn

[a] *LCC-CNRS, 205 route de Narbonne, 31077 Toulouse, France*
e-mail : myrtil.kahn@lcc-toulouse.fr

The synthesis of metal oxide nanoparticles (NPs) from organometallic precursor is a powerful approach to access nanomaterials of controllable size, shape, and surface; parameters of prime importance for their applications.[1] Our organometallic method takes advantage of the exothermic reaction between the precursor and water. This method was first developed with alkyl zinc compounds and isotropic or anisotropic ZnO NPs were achieved. Multi-solublility of these ZnO NPs was obtained using amino-PEG ligands.[2] New hybrid materials,[3] as well as liquid crystal ligands for controlled growth of ZnO NPs were also developed (Figure 1).[4] Importance of the correlation between width and length in the shape analysis of anisotropic nanoparticles was demonstrated using a 2D size plot.[5]

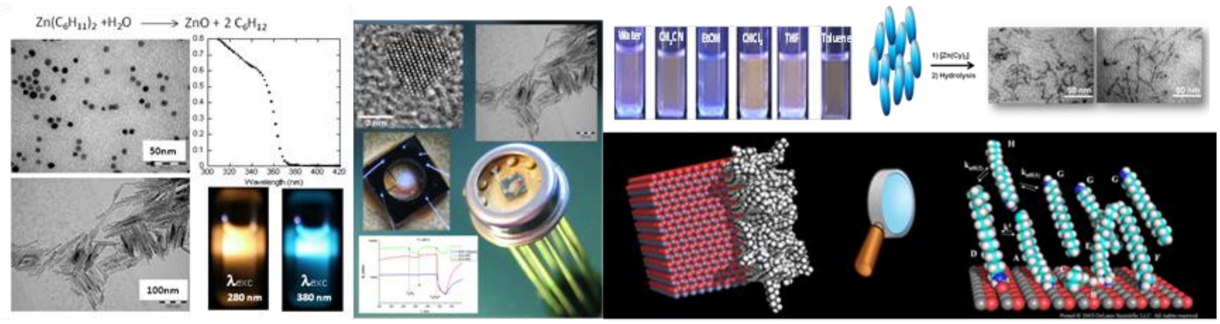


Figure 1. ZnO NPs of isotropic or anisotropic shape, optical properties and their use as gas sensors, multi-solublility properties. Shape control by the use of specific liquid crystal ligands. Full characterization by NPR spectroscopic study.

The full characterization by NMR spectroscopy of the surface of such ZnO NPs stabilized by amine ligands demonstrates that the surface of this apparently simple system is rather complex (Figure 1).[6] Insight into the role of ligands in the yellow luminescence of zinc oxide nanocrystals was investigated.[7] Preparation of other metal oxides (γ-Fe_2O_3, FeO, CoO, $CoFe_2O_4$, CuO, SnO_2) was also achieved and these materials investigated for the development of devices such as nanovaristors,[8] UV detector,[9] IRM contrast agent,[10] and gas sensor[11] (Figure 1).

[1] M. L. Kahn *et al.*, *J. Mater. Chem.*, **2009**, *19*, 4044. [2] J. Rubio-Garcia *et al.*, *ChemCommun*, **2011**, *47*, 988. [3] S. Saliba *et al.*, *J. Mater. Chem.*, **2011**, *21*, 18191. [4] S. Saliba *et al.*, *Angew. Chem. Int. Ed.*, **2011**, *50*, 12032 ; Z. Zheng *et al.*, *Chem. Eur. J.,* **2016**, *22*, 15614. [5] Zhihua Zhao, *et al., Chem. Eur. J.,* **2016**, *22*, 12424 [6] Y. Coppel *et al.*, *Chem. Eur. J.*, **2012**, *18*, 5384 ; Y. Champouret *et al., J. Am. Chem. Soc*, **2016**, *138*, 16322 ; G. Spataro *et al.*, *PCCP*, **2018**, *20*, 12413 [7] G. Spataro, *et al., Eur. J. Inorg. Chem.,* **2016**, 2056 ; [8] M. L. Kahn *et al.*, *Adv. Funct. Mater.*, **2009**, *19*, 1. [9] J. Carrey *et al.*, *Semicond. Sci. Technol*, **2008**, *23*, 025003. [10] G. Casterou, *et al., Chem. Eur. J.*, **2015**, *21*, 18855 ; F. Sciortino *et al., ChemNanoMat.,* **2016**, *2,* 796 ; F. Sciortino *et al., Soft Matter*. **2017**, *13*, 4393 ; F. Sciortino *et al., PCCP*, **2017**, 20, 2761 [11] A. Ryzhikov *et al., J. Nanopart. Res.*, **2015**, *17*, 280 ; J. Jońca *et al., Chem. Eur. J.,* **2016**, *22*, 10127 ; J. Jońca *et al., Sens. Actuator B-Chem,* **2017**, 249, 357 *;* J. Jońca *et al., ChemPhysChem,* **2017**, 18, 2658.

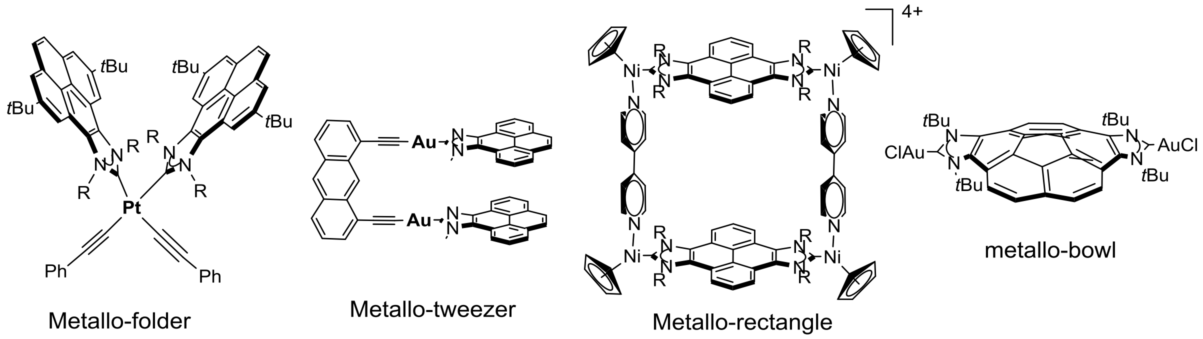
Polyaromatic-adorned N-Heterocyclic Carbenes. From Homogeneous Catalysis to Host-guest chemistry studies

Eduardo Peris

Instituto de Materiales Avanzados (INAM). Universitat Jaume I. 12006 Castellón (Spain).
e-mail: eperis@uji.es

In the course of our most recent research, we demonstrated how homogeneous catalysts with polyaromatic functionalities possess properties that clearly differ from those shown by analogues lacking these polyaromatic systems.[1] The differences arise from the ability of the polyaromatic groups to afford non-covalent interactions with aromatic molecules, which can either be substrates in a homogeneous catalysed reaction, or the same catalysts to afford self-assembled systems.[2]

The development of a wide variety of N-heterocyclic carbene ligands with extended polyaromatic functionalizations also allowed us to prepare a large variety of metallo-supramolecular complexes, including metallotweezers,[3] metallo-rectangles,[4] metallo-folders[5] and bowl-shaped metallo-structures.[6] Depending on their structural features, these species were used for the recognition of a variety of organic substrates, such as electron-deficient aromatic substrates, polycyclic aromatic hydrocarbons and heavy metal cations. The most relevant results in this research will be presented.



Metallo-folder

Metallo-tweezer

Metallo-rectangle

metallo-bowl

Figure 1. Some representative metallo-supramolecules.

1. Peris, E. Polyaromatic N-heterocyclic carbene ligands and pi-stacking. Catalytic consequences. *Chem. Commun.*, **52,** (2016) 5777-5787.
2. Raynal, M., Ballester, P., Vidal-Ferran, A., van Leeuwen, P. W. N. M. Supramolecular catalysis. Part 1: non-covalent interactions as a tool for building and modifying homogeneous catalysts. *Chem. Soc. Rev.*, **43,** (2014) 1660-1733.
3. Ibañez, S., Poyatos, M., Peris, E. Cation-Driven Self-Assembly of a Gold(I)-Based Metallo-Tweezer. *Angew. Chem. Int. Ed.*, **56,** (2017) 9786-9790.
4. Martinez-Agramunt, V., Ruiz-Botella, S., Peris, E. Nickel-Cornered Molecular Rectangles as Polycyclic Aromatic Hydrocarbon Receptors. *Chem. Eur. J.*, **23,** (2017) 6675-6681.
5. Nuevo, D., Gonell, S., Poyatos, M., Peris, E. Platinum-Based Organometallic Folders for the Recognition of Electron-Deficient Aromatic Substrates. *Chem. Eur. J.*, **23,** (2017) 7272-7277.
6. Mejuto, C., Escobar, L., Guisado-Barrios, G., Ballester, P., Gusev, D., Peris, E. Self-Assembly of Di-N-Heterocyclic Carbene-Gold-Adorned Corannulenes on C-60. *Chem. Eur. J.*, **23,** (2017) 10644-10651.

Cyanido-bridged Fe/Co pairs : how to make them and how to study the switching mechanism

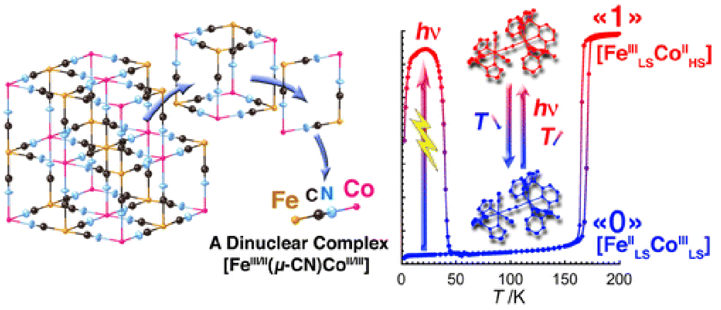
Corine Mathonière

ICMCB, UMR 5026, F-33600 Pessac, France; [2] Univ. Bordeaux, France;

e-mail : corine.mathoniere@icmcb.cnrs.fr

The rational design of molecular systems, which exhibit switchable physical properties as a function of external stimuli (*T*, *E* or *H*, *hv*, *P*, etc.) is a subject of the intense research activity to conceive high-performance molecule-based electronic devices.[1,2] Over the past decade, chemists have investigated the synthesis of magnetic and photoresponsive complexes through rational choices of cyanido-based building blocks. This approach has been extremely successful, and various molecular architectures have been obtained with remarkable properties such as spin crossover,[3] electron-transfer process,[4] and photoinduced magnetism.[4,5] In our quest to obtain new molecular systems and concomitantly to reduce the size of these functional molecules, we reported dinuclear complexes,[6,7] which exhibit switchable optical and magnetic properties due to the thermally and light induced electron transfer in solid state.

In this presentation, the switching properties of the dinuclear complex $[(Tp)Fe^{III}(CN)_3Co^{II}(PY5Me_2)]^+$ (PY5Me$_2$ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine; Tp = hydridotris(pyrazol-1-yl)borate),[7] will be presented using a combination of bulk structural, spectroscopic, magnetic and photomagnetic studies. Moreover, the thermal and light-induced electron transfer process followed at the local level by X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements at Fe and Co $L_{2,3}$ edges will be presented.



[1] O. Sato et al., Angew. Chem. Int. Ed., **2007**, *46*, 2152. [2] C. Simao et al., Nat. Chem., **2011**, *3*, 359; F. Prins et al., Adv. Mater., **2011**, *23*, 1545. [3] M. Nihei et al., Angew. Chem. Int. Ed., **2005**, *44*, 6484; R. Herchel et al., Inorg. Chem., **2004**, *43*, 4103; M. Shatruk et al., J. Am. Chem. Soc., **2007**, *129*, 6104; I. Boldog et al., Inorg. Chem., **2009**, *48*, 3710. [4] D. Li et al., J. Am. Chem. Soc., **2008**, *130*, 252; Y. Zhang et al., Angew. Chem. Int. Ed., **2010**, *49*, 3752; J. Mercurol et al. Chem. Commun., **2010**, *46*, 8995; M. Nihei et al., J. Am. Chem. Soc., **2011**, *133*, 3592; K. E. Funck et al., Inorg. Chem., **2011**, *50*, 2782; Y. Zhang et al., J. Am. Chem. Soc., **2014**, *136*, 16854. [5] A. Bleuzen et al., Inorg. Chem., **2009**, *48*, 3453. [6] I.-R. Jeon et al., Chem. Sci., **2013**, *4*, 2463. [7] E. S. Koumousi et al., J. Am. Chem. Soc., **2014**, *136*, 15461.

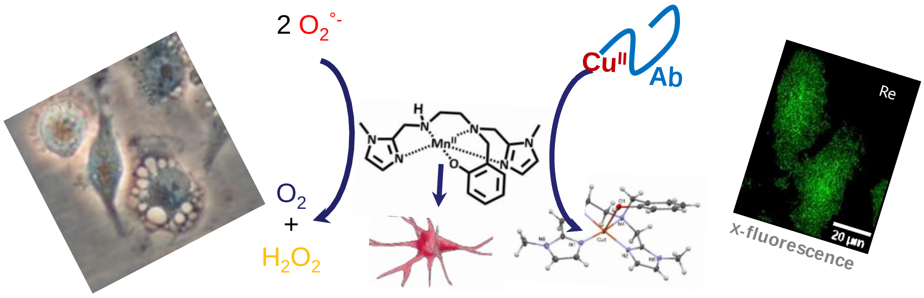
Metal complexes in biological environments: a new frontier in inorganic chemistry

Clotilde Policar,[a] Nicolas Delsuc,[a] Helene Bertrand,[a] Christelle Hureau[b]

[a]Laboratoire des biomolécules, LBM, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France clotilde.policar@ens.fr
[b]CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, France

Metal complexes are increasingly used for biological applications, as metal-centered probes for imaging or as metal-based drugs.[1, 2] To be active a metal complex must reach its biological target that can be buried in cells. Intracellular quantification, speciation of the metal cation, and intracellular distribution through imaging, as well as the evaluation of the activity directly in a cellular environment are key steps in the design, study and rationalization of of metallodrugs. In this talk, we will show how cellular models can be designed to evaluate the activity of metal-based anti-oxidants mimicking the anti-oxidant and cell-protective proteins, superoxide dismutases (SOD). Most of the metal complexes studied in the literature for their bio-activity are used as anti-cancer or anti-bacterial agents, and, because of that, most of the corresponding bio-analyses are focused on toxic effects. In contrast, anti-oxidants and SOD mimics are meant to restore normal functioning of cells by limiting oxidative stress. Specific non-routine strategies are required to characterize their bio-activity.[3-5] We will show how a cellular model can be used to evaluate an intracellular SOD-like activity. An application of a Mn-based SOD mimic (**1**) in the context of Alzheimer disease will then be discussed and we will show how **1** can be used to prevent Cu(II)-induced formation of reactive oxygen species (ROS) in presence of Aß, through a metallic exchange.[6] In a third part, we will show that specific techniques can be used to image metal-based probes. More specifically, probes made of a central metal-CO core, called SCoMPIs (for single core multimodal probes for imaging), can be mapped using unconventional imaging techniques such as IR and X-fluorescence imaging.[7-9]

These three topics have been chosen to exemplify a range of approaches at this new frontier in inorganic chemistry.



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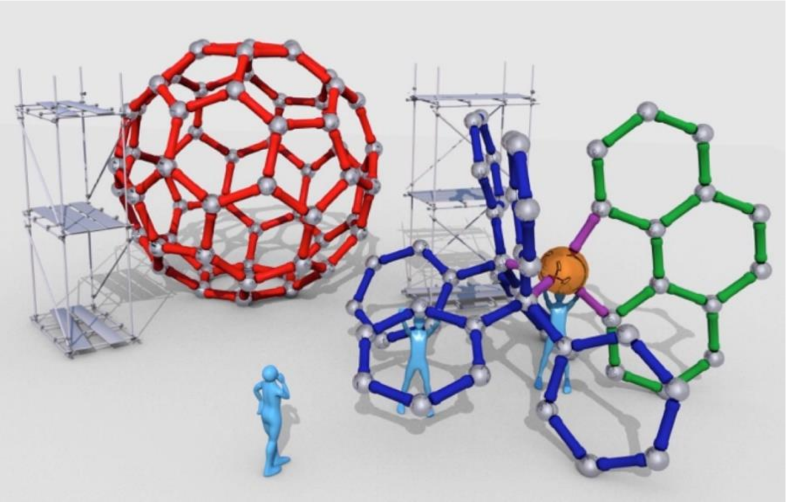
[1] Farrer N. J., Sadler P. J., in: Alessio E., Bioinorganic medicinal chemistry, Medicinal inorganic chemistry: state of art, new trends and vision of the future, Wiley, Weinheim, 2011, pp. 1-47
[2] Gilston B. A., O'halloran T., in: Culotta V., Scott R. A., Metals in cells, Mechanisms controlling the metal economy, Wiley, United Kingdom, 2013,
[3] Mathieu E., Bernard A.-S., Delsuc N., Quévrain E., Gazzah G., Lai B., Chain F., Langella P., Bachelet M., Masliah J., Seksik P., Policar C., Inorg. Chem. 56 (2017) 2545-2555.
[4] Bernard A.-S., Giroud C., Ching H. Y. V., Meunier A., Ambike V., Amatore C., Guille Collignon M., Lemaître F., Policar C., Dalton Trans. 41 (2012) 6399-6403.
[5] Policar C., in: Reboucas J. S., Batinic-Haberle I., Spasojevic I., Warner D. S., St. Clair D., Redox Active Therapeutics, , Springer, Switzerland, 2016, pp. 125-164
[6] Conte-Daban A., Ambike V., Guillot R., Delsuc N., Policar C., Hureau C., Chemistry – A European Journal 24 (2018) 5095-5099.
[7] Hostachy S., Policar C., Delsuc N., Coord. Chem. Rev. 351 (2017) 172-188.
[8] Hostachy S., Masuda M., Miki T., Hamachi I., Sagan S., Lequin O., Medjoubi K., Somogyi A., Delsuc N., Policar C., Chem. Sci. 9 (2018) 4483-4487.
[9] Clède S., Policar C., Chem. Eur. J. 21 (2015) 942 – 958.

From photoactive fullerene-donor conjugates to luminescent copper(I) complexes

Jean-François Nierengarten

Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (LIMA - UMR 7042), ECPM, 25 rue Becquerel, 67087 Strasbourg, France
e-mail : nierengarten@unistra.fr

Coordination compounds possessing low-lying metal-to-ligand charge transfer (MLCT) excited states with marked reducing character are also excellent partners for [60]fullerene in photoactive multicomponent hybrid systems. We have prepared a large number of dyads in which [60]fullerene is coupled with photoactive coordination compounds of Ru(II), Re(I), Ir(III) and Cu(I). For most of these systems, the energy of the lowest triplet MLCT level lies higher than that of the fullerene singlet and triplet, whereas the charge separated state is intermediate. Upon excitation of the metal-complexed moiety, charge separation followed by charge recombination to the fullerene triplet is generally observed. Practically, since direct excitation of the fullerene moiety results in regular deactivation without intercomponent interactions, the fullerene triplet level is the final energy sink of the dyad, whatever the excitation wavelength. The situation is rather different in the case of Cu(I)-bisphenanthroline fullerene hybrids. Cu(I) complexes are indeed stronger reducing agents than Ru(II), Re(I) or Ir(III) systems, thus the charge separated state is the lowest in the energy level diagram, originating a different pattern of photoinduced processes. During the photophysical studies carried out on these dyads, we have also systematically investigated the electronic properties of the corresponding model compounds and thus became progressively involved in the field of phosphorescent metal complexes. In particular, we have developed strongly luminescent Cu(I) complexes and have been among the first to show the potential of such compounds for light emitting applications. Indeed, such non-toxic Cu(I) complexes are interesting alternatives to the heavy metal complexes (Ir(III) and Pt(II) derivatives) typically used as electrophosphorescent materials in LEDs. The most recent advances in this field will be summarized in the present lecture.

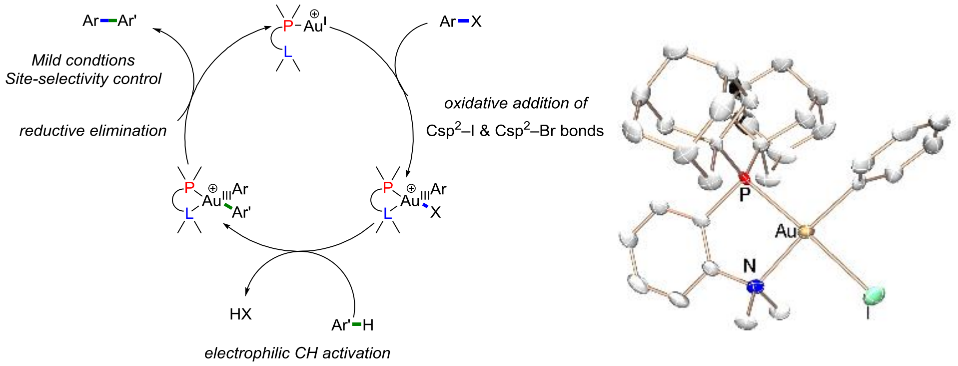


Ligand design in Au(I)/Au(III) chemistry: From fundamental organometallic studies to the development of new gold catalysis.

Abderrahmane Amgoune

Université de Lyon, UCBL, ICBMS UMR 5246, 1 rue Victor Grignard, Villeurbanne, France
e-mail: abderrahmane.amgoune@univ-lyon1.fr

Homogeneous gold catalysis has developed very rapidly over the past ten years, to the extent that gold complexes are now among the most efficient catalytic systems in organic synthesis. However, in contrast to the other transition metals, very little is known about the structure and fundamental reactivity of gold complexes. For instance, oxidative addition which is the common entry point to cross-coupling catalytic cycles, is not favored for gold(I) complexes and was even considered as impossible. Thanks to rational ligand design approaches, we recently showed that this preconception was not true and evidenced that oxidative addition of Csp^2-X and C-C bonds to gold(I) is readily feasible under mild conditions.[1] The first gold-catalyzed direct arylation of (hetero)arenes with aryl halides has been developed,[2] via a rational construction of new Au(I)/Au(III) catalytic cycles. On the other hand, the ligand design approach was also key for the stabilization of previously unknown organometallic compounds with gold(I) and gold(III), allowing the development on new gold catalyzed transformations. [3] The key role of the ligand on the stabilization of highly reactive gold intermediates and on their catalytic behavior will be discussed.



[1]. (a) Joost, M.; Zeineddine, A.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014,** *136*, 14654, (b) M. Joost, L. Estevez, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem., Int. Ed.*, **2015**, *54,* 5236.
[2]. Zeineddine, A.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D *Nature Commun.*, **2017**, *8,* 565.
[3]. (a) Zeineddine,A.; Rekhroukh,F.; Sosa Carrizo,E.D.; Mallet-Ladeira,S.; Miqueu,K.; Amgoune,A.; Bourissou,D. *Angew. Chem. Int. Ed.*, **2018**, 57, 1306, (b) C. Blons, S. Ladeira, A. Amgoune, D. Bourissou, *Angew. Chem., Int. Ed.*, **2018**, *57,*11732.

Communications
Orales

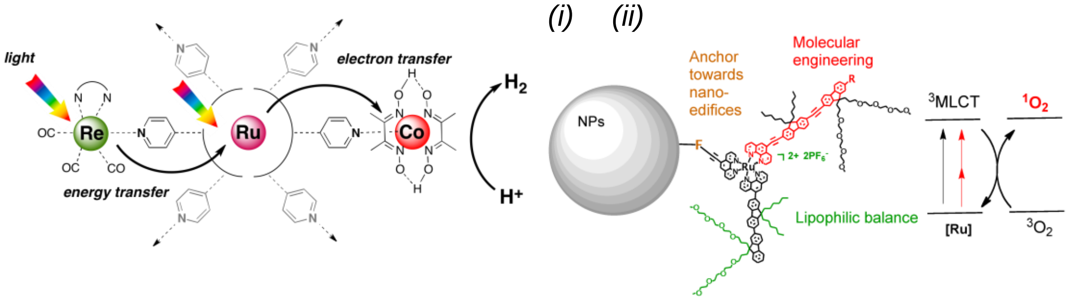
On the use of ruthenium(II) polypyridyle building blocks in linear and non-linear optical systems

Elodie Rousset,[a,b,c] Sylviane Chevreux,[a] Garry Hanan,[b] Valerie Marvaud,[c] Gilles Lemercier.[a]

[a] Université de Reims Champagne Ardenne,
ICMR UMR CNRS 7312 BP 1039 – 51687 Reims cedex 2, France
[b] Département de Chimie, Université de Montréal,
2900 Edouard-Montpetit, Montréal, Québec H3T-1J4,
[c] UPMC-Sorbonne Université,
IPCM-CNRS-8232cc 42, 4 place Jussieu, 75252 Paris Cedex 05, France.

e-mail : gilles.lemercier@univ-reims.fr, elodie.rousset@univ-reims.fr

The valuable photophysical properties of the archetypal $[Ru(bpy)_3]^{2+}$, and the tremendous number of its analogues, have no longer to be proven. Our research interest lies in the use of such derivatives as functional subunits to design optically-active complex systems.[1] Based on the linear or nonlinear character of the optical response, a great range of potential applications becomes accessible, from environmental concerns to public health issues. We will address in particular: (*i*) their use as photosensitzers in supramolecular artificial photosynthesis assemblies where conversion of sunlight and water into H_2 is based on the appropriate combination with other functional subunits as chromophores, and catalysts. [2, 3] (*ii*) linear and two photon absorption properties of new 5-(fluorenyl)-1,10-phenanthroline based Ru(II) complexes[4] in the perspective of potential applications such as optical power limiting[5] or two-photon excited photodynamic therapy (2PE-PDT).[6]
We will then present one of our approach towards the elaboration and study of related functionalized nanoparticles[1] and more particularly a switch from two-photon absorption of Ru(II) coordination complexes in solution to a saturable absorption phenomena for the related decorated-gold nanoparticles.[7]



[1] G. Lemercier, M. Four, S. Chevreux, *Coord. Chem. Rev.*, **2018**, *368*, 1.
[2] E. Rousset, D. Chartrand, I. Ciofini, V. Marvaud, G. S. Hanan, *Chem. Comm.*, **2015**, *51*, 9261.
[3] E. Rousset, I. Ciofini, V. Marvaud, G. S. Hanan, *Inorg. Chem.*, **2017**, *56*(16), 9515.
[4] O. Mongin, M. Four, S. Chevreux, M. Blanchard-Desce, G. Lemercier, *Chimia*, **2015**, *69*, 666.
[5] M. Four, D. Riehl, O. Mongin, M. Blanchard-Desce, L. M. Lawson-Daku, J. Moreau, J. Chauvin, J. A. Delaire, G. Lemercier, *PhysChemChemPhys.*, **2011**, *13*, 17304.
[6] C. Boca, M. Four, A. Bonne, B. van Der Sanden, S. Astilean P. L. Baldeck, G. Lemercier, *Chem. Commun.*, **2009**, 4590.
[7] J. Moreau, F. Lux, M. Four, J. Olesiak-Banska, K. Matczyszyn, P. Perriat, C. Frochot, P. Arnoux, O. Tillement, M. Samoc, G. Ponterini, S. Roux, G. Lemercier, *Phys. Chem. Chem. Phys* , **2014**, *16*,14826.

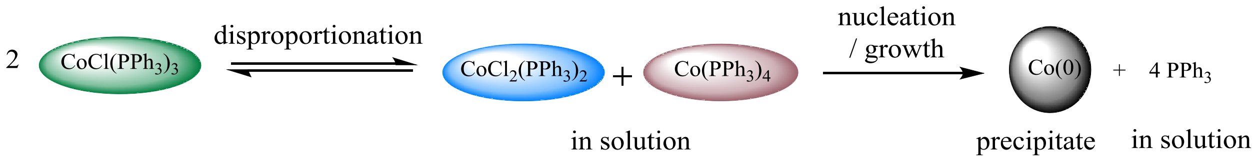
Theoretical study of Reduction Routes of $MX(PPh_3)_3$ in complex environment toward synthesis of Cobalt and Nickel Nanocrystals

Maya Guillaumont,[a] Hélène Gérard[a], Stéphanie Halbert[a], Marc Petit[b], Christophe Petit[c]

[a] Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT UMR 7616, F-75005 Paris, [b] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM UMR 8232, F-75005 Paris, [c] Sorbonne Université, CNRS, MONARIS UMR 8233, F-75005 Paris
E-mail: maya.guillaumont@lct.jussieu.fr

Keywords: Cobalt; Nickel; Disproportionation; DFT

Starting from a $CoCl(PPh_3)_3$ complex, synthesis of monodisperse hcp Cobalt nanoparticles[1] takes place through an original disproportionation path. In this presentation we unravel, toward computational studies of simple models, the role of the oleylamine solvent, the nature of phosphine ligands, and of the halogen anion. Our synergetic computational and experimental analysis provide better understanding on the redox behavior of Cobalt in complex environment, highlighting how nanoparticles formation occurs upon a fine balance of the stabilization of several oxidation degrees and coordination numbers[2] of the metal center. Finally, comparisons to other reduction routes or other metal precursors (Ni, Cu) point out the numerous competing processes possibly at stake in this experimental procedure.



Key steps toward synthesis of Cobalt nanocrystals in solution

[1] Meziane, L.; Salzemann, C.; Aubert, C.; Gérard, H.; Petit, C.; Petit, M. *Nanoscale* **2016**, *8,* 18640–18645.
[2] In revision : Vivien, A ; Guillaumont, M ; Meziane, L.; Salzemann, C.; Aubert, C.; Halbert, S. ; Gérard, H.; Petit, M.; Petit, C. *Chem. Mater.*

Hierarchichal self-assembly of polyoxometalate-based hybrids driven by metal coordination and electrostatic interactions

Guillaume Izzet,[a] Madeleine Piot,[a] Raphaël Salles,[a] Anna Proust.[a]

[a] *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, 4 Place Jussieu, F-75005 Paris.*
e-mail : guillaume.izzet@sorbonne-universite.fr

Polyoxometalates (POMs) are a class of discrete metal oxo clusters that bridge the gap between small oxo-metal complexes and bulk metal-oxides.[1] Owing to their nanoscale size, their structural complexity and their sensitivity to various types of interactions, POMs are attractive molecular building units for the elaboration of complex molecular assembly with emergent properties. In this context, we are developing mesoscopic POM-based nanostructures via metal-directed self-assembly processes.[3,4] The approach relies on the synthesis of POM-based building blocks bearing remote binding functions with well-suited orientations and denticities (Figure 1, left). Coordination of these hybrid building blocks to complementary metal ions afford various self-assembled architectures from discrete coordination oligomers to 2D networks. Owing to the ionic character of POMs, the primary self-assembled systems may further aggregate through intermolecular electrostatic interactions and afford larger multi-scale assemblies (Figure 1, right).[5,6] This presentation will focus on the synthesis and characterization of the different POM-based self-assemblies. An important emphasis will be devoted to the control of the shape of the hierarchichal nano-assemblies.

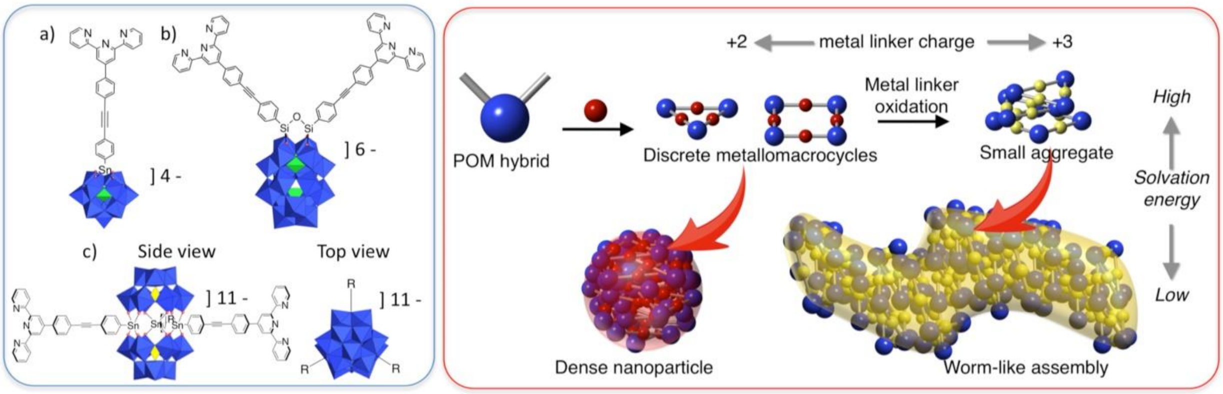


Figure 1. Left: Representation of different types of POM-based building blocks. a) monotopic; b) ditopic; c) tritopic hybrids. Right**:** Schematic representation of the formation of the nanosized aggregates by hierarchical metal driven self-assembly of a ditopic POM-based building block according to the solvent composition and the metal linker charge.

[1]. A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh, G. Izzet, *Chem. Soc. Rev.*, **2012**, 7605–7622.
[2]. G. Izzet, F. Volatron, A. Proust, A. *Chem. Rec.* **2017**, *17*, 250–266.
[3]. G. Izzet, A. Macdonell, C. Rinfray, M. Piot, S. Renaudineau, E. Derat, B. Abécassis, C. Afonso, A. Proust, *Chem. Eur. J.* **2015**, *21*, 19010–19015.
[4]. M. Piot, S. Hupin, H. Lavanant, C. Afonso, L. Bouteiller, A. Proust, G. Izzet, *Inorg. Chem.,* **2017**, *56*, 8490−8496.
[5]. G. Izzet, B. Abécassis, D. Brouri, M. Piot, B. Matt, S. A. Serapian, C. Bo, A. Proust, *J. Am. Chem. Soc.* **2016**, 138, 5093-5099.
[6]. M. Piot, B. Abécassis, D. Brouri, C. Troufflard, A. Proust, G. Izzet**,** *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *36*, 8895-8900.

New way to rectify current thanks to Ferrocenyl Triazole derivatives

Damien Brunel,[a] Clément Reynaud,[b] David Duché,[b] Ludovic Escoubas,[b] Didier Gigmes,[a] Frédéric Dumur[a]

[a]Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille (France).
[b]Aix Marseille Univ, CNRS, Institut Nanomatériaux Microélectronique Nanosciences de Provence, UMR 7334, F-13397 Marseille (France)
e-mail : damien.brunel@univ-amu.fr

Rectification of current by molecules is a subject that attracts many attentions nowadays because it would permit to reduce the size of the electronic devices. Theorized by Aviram and Ratner, the rectification can be achieved by an asymmetric molecule, enabling the electrons to be transferred in a preferential direction through the molecule. The state of the art of the organic molecular rectifiers shows rectification ratios up to 10^5. [1] Such rectification ratios were obtained with molecules composed of a ferrocene, which is the key of the rectification process, linked to an insulating alkyl chain. At present, not so much efforts have been devoted to control the orientation of the molecular rectifiers, relative to the electrode (See Figure 1). In our case, such a control of the molecular orientation has been obtained by a two-step process based on Click Chemistry. [2]

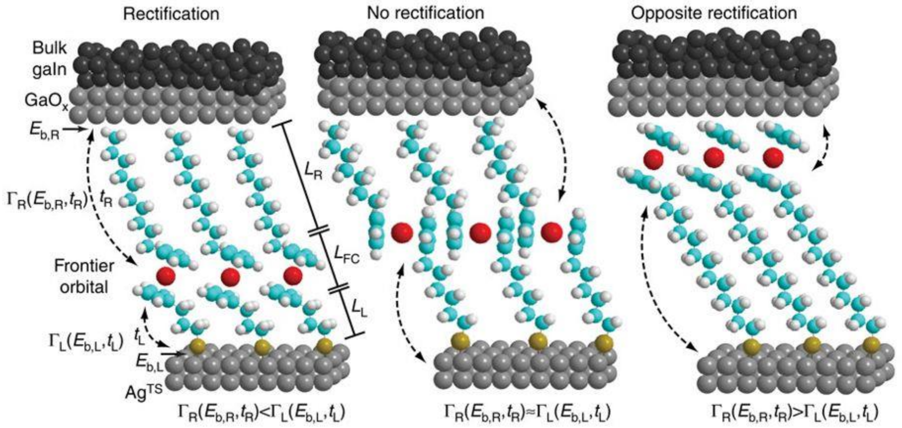


Figure 1. Importance of position of ferrocene in the rectification

Here, we present unprecedented works on the synthesis of new ferrocene derivatives designed as molecular rectifiers. Especially, a special effort is devoted: firstly, to allow the molecule to be covalently linked to an electrode and secondly to definitely control the orientation of the molecular rectifier relative to the electrode.

[1] Chen, X.; Roemer, M.; Yuan, L.; Du, W.; Thompson, D.; del Barco, E.; Nijhuis, C. A., *Nat. Nanotechnol*. **2017**, *12*, 797.
[2] Yuan, L.; Nerngchamnong, N.; Cao, L.; Hamoudi, H.; del Barco, E.; Roemer, M.; Sriramula, R. K.; Thompson, D.; Nijhuis, C. A, *Nat. Commun*. **2015**, *6*, 6324.

Binuclear *µ-nitrido* iron complexes for nitrene transfer in catalysis

Jordan Donat,[a] Jacques Pécaut,[b] Jean-Marc Latour.[a]

[a] *CEA/DRF/BIG/LCBM, CEA-Grenoble, 17 rue des Martyrs 38054 Grenoble Cedex, France·*
[b] *CEA/DRF/INAC/SYMMES, CEA-Grenoble, 17 rue des Martyrs 38054 Grenoble Cedex, France·*

e-mail : jordan.donat@cea.fr

µ-nitrido diironphtalocyanine and diironporphyrin complexes ($PcFe^{III}$-N-$Fe^{IV}Pc$ and $PorFe^{III}$-N-$Fe^{IV}Por$) exhibit the remarkable property to catalyze methane oxidation by H_2O_2 in water in mild conditions[1]. The *µ-nitrido* bridge plays an essential role in the electronic delocalization between the two Fe ions and in the enhancement of the basicity of the iron which is crucial for $H^{\bullet}$ abstraction[2]. To further assess the role of this peculiar bridge and enlarge the reactivity scope of these binuclear complexes we have endeavored to associate two iron macrocycles of different origins. As an initial attempt we choose to associate an iron porphyrin with a Fe complex of a tetracarbido (NHC) macrocycle[3]. Indeed the strong σ donor character of the latter ligand is likely to strongly influence the oxidative reactivity of the dinuclear complex.

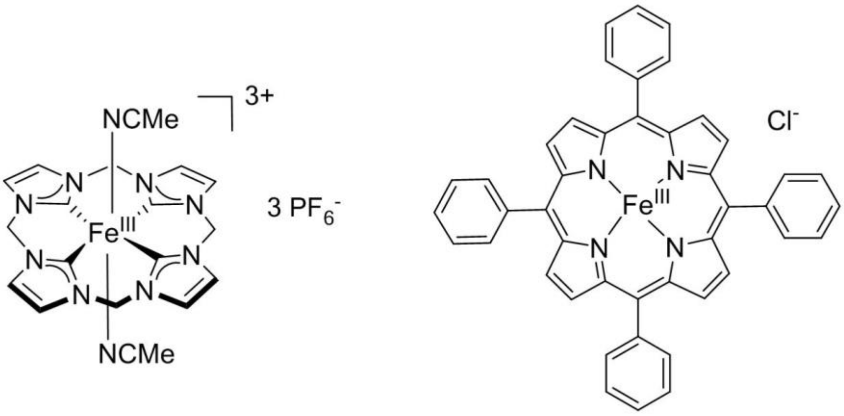


Figure 1

In this communication, we present our attempts to couple an iron tetraphenylporphyrin with the Fe complex of the simplest N-heterocyclic tetracarbene (Figure1).

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[1] A.B. Sorokin, E.V. Kudrika, D. Bouchu, *ChemComm*, **2008**, 2562–2564.
[2] E.V. Kudrik, P. Afanasiel, L.X. Alvarez, P. Dubourdeaux, M, Clémancey, J.-M, Latour, G. Blondin, D. Bouchu, F. Albrieux, S.E. Nefedov, A.B. Sorokin, *Nature Chemistry*, **2012**, *4*, 1024-1029.
[3] M.R. Anneser, S. Haslinger, A. Pöthig, M. Cokoja, J.-M. Basset, F.E. Kühn *Inorg.Chem*, **2015**, *54*, 3797−3804.

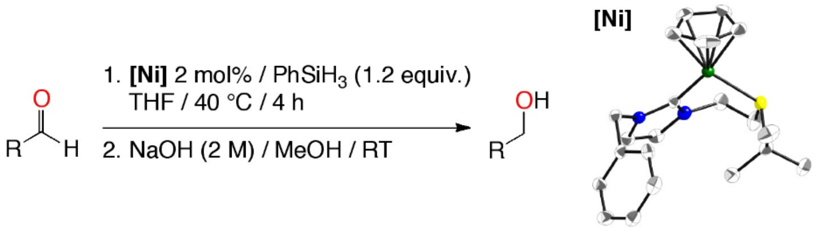
Synthesis and application in aldehyde hydrosilylation of nickel(II) complexes bearing hemilabile thioether-functionalised NHC ligands

Franck Ulm,[a] Amalia I. Pobaldor-Bahamonde,[b] Michael J. Chetcuti,[a] Thierry Achard,[c] Vincent Ritleng[a]

[a] Université de Strasbourg, Laboratoire d'Innovation Moléculaire et Applications, UMR CNRS 7042, 25 rue Becquerel, 67087 Strasbourg. [b] Université de Genève, Département de Chimie Organique, 30 Quai Ernest Ansermet, 1211 Genève, Suisse. [c] Université de Strasbourg, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR CNRS 7504, 23 rue du Loess, 67000 Strasbourg.
e-mail : franck.ulm@etu.unistra.fr

Nickel–NHC complexes have become an important class of precatalysts over the last ten years principally due to the widespread trends to replace noble metals by less expensive and earth abundant 3d metals, and phosphine ligands by the less nocuous N-heterocyclic carbenes (NHC), as well as the intrinsic fascinating reactivity of nickel.[1] Nevertheless, some important limitations still remain that need to be overcome before foreseeing the replacement of palladium-based systems by nickel. The main challenges include (i) the decrease of the catalyst loadings, (ii) the use of milder reaction conditions, and (iii) the use of less sensitive precatalysts. A possible answer to these challenges lies with the development of well-defined nickel(II) precatalysts with fine-tuned stereo-electronic properties.

Efforts from our group have been directed toward the diversification of pseudo-trigonal [Ni(η^5-C_5R_5)L(NHC)]$^{(+)}$ complexes, and the study of their catalytic activity in a variety of reactions, including C–heteroatom multiple bond hydrosilylation.[2] More recently, a related cyclometalated pyridyl-functionalized triazolylidene NiCp was reported to reach TOFs of up to 13 350 h^{-1}.[3] This very high activity was attributed to a well-balanced hemilabile *C,N*-chelation. In this context, we wondered whether a thioether-functionalised NHC could provide a suitable balance in nickel-catalysed reactions. Indeed, among the variety of potentially hemilabile groups containing a donor atom (N, O, P and S) that have been introduced at the N atoms of NHCs, thioether-functionalized NHCs remain a marginal class of ligands.[4] Yet the weaker coordinating ability of the thioether moiety to nickel makes them perfect candidates for hemilabile systems in catalysis. In this communication, we will describe the first nickel complexes bearing κ^2-*C,S*-thioether-functionalised NHCs, [NiCp{R-NHC-$(CH_2)_2$SR'}](PF_6) and their κ^1-C precursors, [NiCpBr{R-NHC-$(CH_2)_2$SR'}]. The sulphur coordination to nickel was studied by a combination of VT ^{1}H NMR experiments, X-ray diffraction studies and DFT calculations. Of notable interest, the cationic κ^2-*C,S* species proved more active than their neutral κ^1-*C* analogues for the hydrosilylation of aldehydes.[5]



[1] S. Z. Tasker, E. A. Standley and T. F. Jamison, *Nature* **2014**, *509*, 299; V. Ritleng, M. Henrion, M. J. Chetcuti, *ACS Catal.* **2016**, *6*, 890; *ACS Catal.* **2015**, *5*, 1283.
[2] L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J.-B. Sortais, V. Ritleng, *Adv. Synth. Catal.*, **2012**, *354*, 2619 ; *Catal. Sci. Technol*. **2013**, *3*, 3111.
[3] Y. Wei, S.-X. Liu, H. Mueller-Bunz, M. Albrecht, *ACS Catal.* **2016**, *6*, 8192.
[4] M. Bierenstiel, E. D. Cross, *Coord. Chem. Rev.* **2011**, *255*, 574; D. Yuan, H. V. Huynh, *Molecules*, **2012**, *17*, 2491; C. Fliedel, P. Braunstein, *J. Organomet. Chem.* **2014**, *751*, 286.
[5] F. Ulm, A. I. Poblador-Bahamonde, S. Choppin, S. Bellemin-Laponnaz, M. J. Chetcuti, T. Achard, V. Ritleng, *Dalton Trans.* **2018**, DOI: 10.1039/c8dt03882a.

Interdigitation for the elaboration of conducting MOFs

Damien Bechu,[a] Lilia Xie,[b] Stéphane Baudron,[a] Sylvie Choua,[c] Mircea Dinca,[b] Mir Wais Hosseini.[a]
[a] Université de Strasbourg, UMR-CNRS 7140, Laboratoire de Tectonique Moléculaire, 4 rue Blaise Pascal, 67000 Strasbourg, France
[b] Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States
[c] Université de Strasbourg, UMR-CNRS 7177, Laboratoire POMAM, 4 rue Blaise Pascal, 67000 Strasbourg, France
E-mail: damien.bechu@etu.unistra.fr

Metal organic frameworks (MOFs) have been developed over the few decades for various applications such as gas sorption, separation and catalysis.[1–3] More recently, they have also been investigated for their use in the area of opto-electronic and electronic devices.[4] Thus, attention has been drawn to the design of MOFs featuring magnetic properties, luminescence or electronic conductivity.[5–7] In this context, several approaches for charge transport in conducting MOFs have been studied,[5] in particular aiming at either hopping or band transport. Conductivity by band transport or “though space” can be generated using organic linkers which are redox active and prone to π-stacking, such as tetrathiafulvalene (TTF).

In this contribution, we will present our strategy to control the relative arrangement of TTFs in a MOF using the principles of molecular tectonics (Figure).[8] Our strategy relies on the formation of coordination polymers and the promotion of their interdigitation (Figure) or interpenetration. The synthesis and characterization of one material will be discussed.

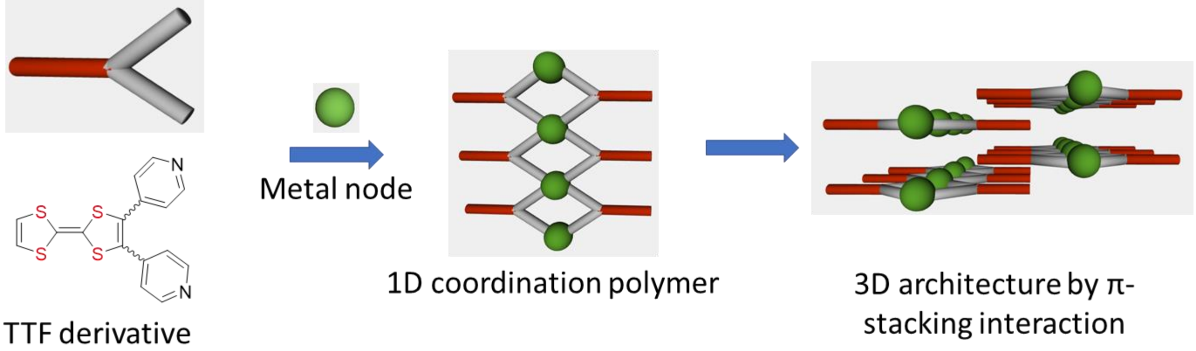


Figure 1. Strategy for the formation of an interdigitated TTF-MOF

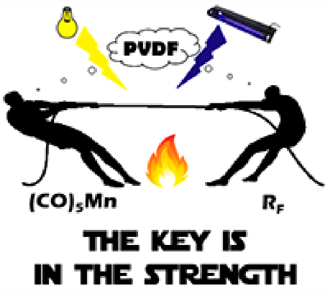
[1] Y. He, W. Zhou, G. Qian and B. Chen, *Chem. Soc. Rev.*, **2014**, *43*, 5657–5678.
[2] J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, **2012**, *112*, 869–932.
[3] P. García-García, M. Müller and A. Corma, *Chem. Sci.*, **2014**, *5*, 2979–3007.
[4] V. Stavila, A. A. Talin and M. D. Allendorf, *Chem. Soc. Rev.*, **2014**, *43*, 5994–6010.
[5] L. Sun, M. G. Campbell and M. Dincă, *Angew. Chem. Int. Ed.*, **2016**, *55*, 3566–3579.
[6] Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, **2012**, *112*, 1126–1162.
[7] P. Dechambenoit and J. R. Long, *Chem. Soc. Rev.*, **2011**, *40*, 3249–3265.
[8] M. W. Hosseini, *Acc. Chem. Res.*, **2005**, *38*, 313–323.

Nouveaux complexes fluoroalkyles $[Mn(R_F)(CO)_5]$: force homolytique, génération de radicaux fluoroalkyles et α-F élimination

Roberto Morales-Cerrada,[a,b] Christophe Fliedel,[a] Jean-Claude Daran[a], Florence Gayet,[a] Vincent Ladmiral,[b] Bruno Améduri,[b] Rinaldo Poli[a]

[a] CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT, 205 Route de Narbonne, F-31077 Toulouse Cedex 4, France. [b] CNRS ; UMR 5253 ; ICGM, Université de Montpellier, CNRS, ENSCM, 240 av du Professeur Emile Jeanbrau, 34296 Montpellier, France
e-mail : rinaldo.poli@lcc-toulouse.fr

Dans le cadre de la polymérisation radicalaire contrôlée du fluorure de vinylidène (VDF) par transfert d'atome de iode,[1] il a été montré que des radicaux $[Mn(CO)_5]^\bullet$, engendrés par activation photochimique de $[Mn_2(CO)_{10}]$, libèrent les chaines radicalaires « tête » ($PVDF\text{-}CH_2CF_2^\bullet = PVDF_H^\bullet$) et « queue » ($PVDF\text{-}CF_2CH_2^\bullet = PVDF_T^\bullet$) des espèces dormantes PVDF-I.[2] L'éventuelle formation d'espèces organométalliques $PVDF_H\text{-}Mn(CO)_5$ et $PVDF_T\text{-}Mn(CO)_5$ n'a pas été validée dans cette étude. Nous avons sondé cette possibilité par la synthèse de complexes modèles et par leur étude thermique. Les nouveaux complexes $[Mn(R_F)(CO)_5]$ ($R_F = CH_2CF_3$, CF_2CH_3),[3] ainsi que les analogues avec $R_F = CF_3$ et CHF_2 déjà décrit dans la bibliographie,[4] ont été synthétisés et complètement caractérisés. L'analyse détaillée des bandes de vibration dans la région des élongations des ligands carbonyles, en conjonction avec des calculs DFT des fréquences de vibration, a permis l'attribution des fréquences des isotopomères $[Mn(R_F)(^{12}CO)_4(eq\text{-}^{13}CO)]$ et $[Mn(R_F)(^{12}CO)_4(ax\text{-}^{13}CO)]$. La rupture homolytique de la liaison R_F-Mn a été étudiée expérimentalement par une méthode cinétique avec piégeage du radical $R_F^\bullet$ par le tris(triméthylsilyl)silane (TTMSS). Les $\Delta H^\ddagger$ ainsi déterminées sont en très bon accord avec les enthalpies thermodynamiques de rupture homolytique (*bond dissociation enthalpy*, BDE) calculées par DFT.[5] La génération de radicaux $R_F^\bullet$, dans des conditions thermiques ainsi que photochimiques (rayonnement visible ou UV), a été validée par l'amorçage de la polymérisation radicalaire du VDF[3] ainsi que de la copolymérisation radicalaire alternée de l'acétate de vinyle et du $CH_2=C(CF_3)COO\mathit{t}Bu$. Enfin, la détermination des sous-produits engendrés lors de la décomposition thermique des dérivés $[Mn(R_F)(CO)_5]$ a mis en évidence un phénomène inédit : l'échange H/F par le TTMSS, sélectivement en position α de la chaine R_F, avec formation de TMS_3SiF. Ainsi, le composé $[Mn(CF_3)(CO)_5]$ génère également, outre le CF_3H attendu, CH_2F_2 et CH_3F ; le composé $[Mn(CHF_2)(CO)_5]$ engendre CH_3F, outre CH_2F_2 ; $[Mn(CH_2CF_3)\text{-}(CO)_5]$, en revanche, ne donne pas lieu à échange H/F. Le mécanisme de cette réaction comporte la dissociation d'un ligand CO suivie par une α-F élimination, comme montré par une étude DFT détaillée.[6]



[1] G. David, C. Boyer, J. Tonnar, B. Améduri, P. Lacroix-Desmazes, B. Boutevin, *Chem. Rev.* **2006**, *106*, 3936-3962.
[2] A. D. Asandei, O. I. Adebolu, C. P. Simpson, *J. Am. Chem. Soc.* **2012**, *134*, 6080-6083.
[3] R. Morales-Cerrada, C. Fliedel, J.-C. Daran, F. Gayet, V. Ladmiral, B. Améduri, R. Poli, *Chem. Eur. J.* **2018**, https://doi.org/10.1002/chem.201804007.
[4] K. Noack, U. Schaerer, F. Calderazzo, *J. Organometal. Chem.* **1967**, *8*, 517-526.
[1] R. Poli, S. M. W. Rahaman, V. Ladmiral and B. Améduri, *J. Organomet. Chem.* **2018**, *864*, 12-18
[6] R. Morales-Cerrada, C. Fliedel, F. Gayet, V. Ladmiral, B. Améduri, R. Poli, *Organometallics*, accepté.

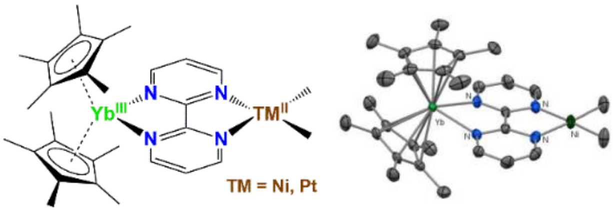
Synthesis and Characterizations of an Original Heterobimetallic Nickel Complex with Divalent Organolanthanides

Ding Wang,[a] Violaine Goudy,[a] Jules Moutet,[a] Marie Cordier,[a] Grégory Nocton.[a]*

[a] *LCM, Ecole polytechnique, CNRS, Université Paris-Saclay, Route de Saclay, 91128, Palaiseau cedex, France.*
e-mail : ding.wang@polytechnique.edu

Divalent lanthanide complexes have been developed since the 60’s and are comprehensively studied on their electron transfer properties with diverse N-heterocyclic adducts[1]. Our group has discovered related reactivity on divalent organolanthanides with redox non-innocent ligands such as reversible C-C coupling formation[2] or C-H activation[3]. These examples indicate that their ground states play a significant role in impacting the reactivity due to the strong electron correlation provided by redox active ligands[4].

Therefore, an original heterometallic system containing the divalent organolanthanides, redox non-innocent ligands and reactive transition metals such as that in Group 10 has been recently developed in our group[5]. In this system, an electron transfer occurs from the organolanthanides to the transition metal centre. For instance, high-valent Pd^{IV} has been successfully stabilized, which is considered as unstable and undergoing reductive elimination very fast. In this work, we will present a new heterobimetallic Yb-Ni complex with full characterizations by NMR, XRD, and Magnetism, highlighting an interesting electronic structure, as well as reactivity leading to the investigation of some typical organometallic mechanisms[6].



Scheme 1. ORTEP of Cp*$_2$Yb(bipym)NiMe$_2$

The authors thank the European Research Council (ERC) for the grant (No. 716314).

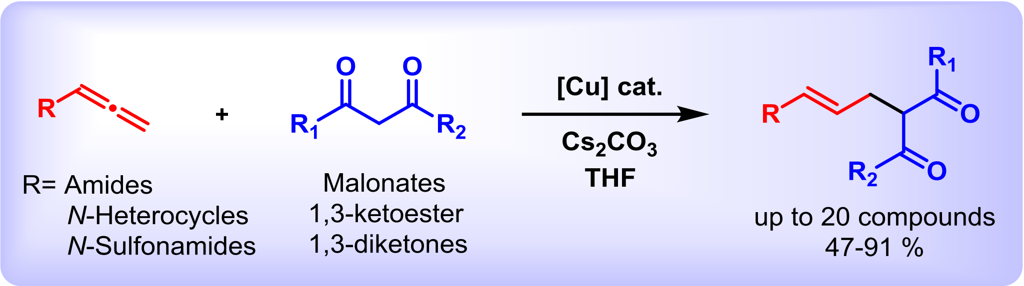
[1]. C. H. Booth, M. D. Walter, D. Kazhdan, Y.-J. Hu, W. W. Lukens, E. D. Bauer, L. Maron, O. Eisenstein, R. A. Andersen, *J. Am. Chem. Soc.* **2009**, *131*, 6480.
[2]. G. Nocton, W. L. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen, *J. Am. Chem. Soc.*, **2014**, *136*, 8626.
[3]. G. Nocton, C. H. Booth, L. Maron, R. A. Andersen, *Organometallics* **2013**, *32*, 5, 1150.
[4]. P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794.
[5]. V. Goudy, A. Jaoul, M. Cordier, C. Clavaguéra, G. Nocton, *J. Am. Chem. Soc.* **2017**, *139*, 10633.
[6]. *manuscript in preparation*

Regio- and Stereoselective Copper-Catalyzed Allylation of 1,3-dicarbonyl compounds with Terminal Allenes

Racha Abed Ali Abdine, [a] Rémi Blieck, [a] Marc Taillefer, [a] Florian Monnier [a,b]

[a]Ecole Nationale Supérieure de Chimie de Montpellier, Institut Charles Gerhardt Montpellier UMR 5253, 8 rue de l'école Normale, 34296 Montpellier, cedex 5 France
[b]Institut Universitaire de France, IUF, 1 rue Descartes, 75231 Paris cedex 5, France
e-mail : racha.abed-ali-abdine@enscm.fr

Allenes compounds have gained an attention in the organic chemistry in the reason of their reactivity. They were able to couple with several nucleophiles to afford the corresponding allylic compounds with a total atom-economy mode. [1]
The reaction of allenes with different carbon pronucleophiles such Meldrum's acid, malonate and β-ketoester was developed using Pd [2] as catalyst or AgF [3] in stoichiometric amount. In this work, we describe the addition of 1, 3-dicarbonyls compounds to *N*-allenyl derivatives using a copper-catalyzed system and through a ligand free system. This methodology presents the first allylation of this kind of pronucleophiles with allenes catalyzed by copper, providing the selective linear allylic product. [4]



Cu-catalyzed allylation of 1,3-dicarbonyl compounds

[1]. a) Koschker, P. Breit, B. Acc. *Chem. Res*. **2016**, *49*, 1524. b) Nunoz, M. P. *Chem. Soc. Rev*. **2014**, *43*, 3164.
[2]. a) Trost, B. M. Gerusz, V. *J. Am. Chem. Soc*. **1995**, *117*, 5156. b) Besson, L. Goré, J. Cazes, B. *Tetrahedron* Lett., **1995**, *36*, 3853
[3]. Wei, T. xie, M.-S. Qu, G.-R. Niu, H-Y. Guo, H.-M. *Org. Lett*., **2014**, *16*, 900
[4]. Blieck, R. Abdine, R. Taillefer, M. Monnier, F. *Org. Lett*., **2018**, *20*, 2232

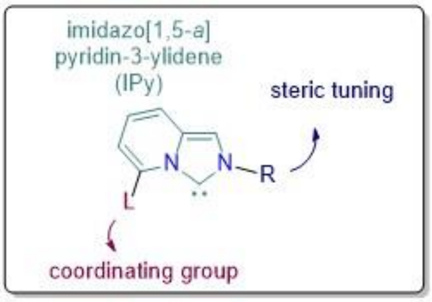
Functionalized imidazo[1,5-a]pyridin-3-ylidene (IPy) ligands: Synthesis, coordination chemistry and catalysis.

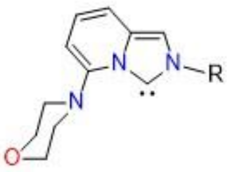
Stéphanie Bastin,*[a] Idir Benaissa,[a] Mathieu Huynh,[a] Marie-Emilie Morantin,[a] Yue Tang,[b] Noël Lugan,[a] Véronique Michelet*[b] and Vincent César*[a]

[a] Laboratoire de chimie de coordination du CNRS (LCC-CNRS), 205 route de Narbonne, BP44099, 31077 Toulouse cedex 4. [b] Université Côte d'Azur, Institut de Chimie de Nice, UMR7272 CNRS, Parc Valrose, Falculté des Sciences, 06100 Nice.
e-mail : stephanie.bastin@lcc-toulouse.fr

N-Heterocyclic Carbenes (NHCs) are now recognized as ubiquitous and powerful ligands in organometallic chemistry and catalysis as well as excellent organocatalysts on their own right.[1] Whereas the research in this domain is still largely dominated by imidazol(in)-2-ylidene type carbenes, we have been recently developing new generations of functionalized NHCs based on the imidazo[1,5-a]pyridin-3-ylidene (IPy) framework. Although disclosed in 2005,[2] this family of bicyclic NHCs has been only seldom studied up to now, mainly due to synthetic limitations.[3] The main advantage of this rigid bicyclic structure is to force the distal L group in close proximity to the metallic center, leading *a priori* to a stronger metal-ligand interaction or to a more efficient chiral transfer if the R group is chiral.

In this communication, we present the chemistry of the three new NHCs **1**, **2** and **3**$^-$, bearing a morpholine, an iminophosphorane and an anionic 'malonate' unit as L group respectively. The imidazo[1,5-a]pyridinium precursors **1**·HBr, **2**·HOTf and **3**·H were easily obtained on gram scale using a new, highly modular, divergent, and versatile synthetic strategy. Their coordination chemistry towards metallic centers will be then presented, as well as the implementation of the resulting pre-catalysts in homogeneous catalysis.[3]





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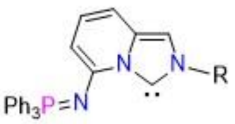

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3$^-$

Acknowledgments

Support by the CNRS and the ANR (grant ANR-16-CE07-0006-03, GOLDWAR) is gratefully acknowledged.

[1] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485-496.
[2] (a) M. Alcarazo, S. J. Roseblade, A. R. Cowley, R. Fernández, J. M. Brown, J. M. Lassaletta, *J. Am. Chem. Soc.* **2005**, *127*, 3290-3291; (b) C. Burstein, C. W. Lehmann, F. Glorius, *Tetrahedron* **2005**, *61*, 6207-6217.
[3] J. Iglesias-Siguenza, C. Izquierdo, E. Diez, R. Fernandez, J. M. Lassaletta, *Dalton Trans.* **2016**, *45*, 10113-10117.

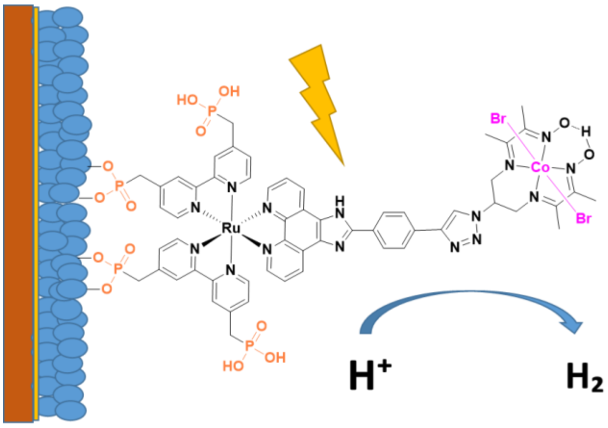
A new RuCo dyad for dye-sensitized hydrogen-evolving photocathode applications

Emmanouil Giannoudis, N. Queyriaux, V. Artero, Murielle Chavarot-Kerlidou

Laboratoire de Chimie et Biologie des Métaux, Univ. Grenoble Alpes, CNRS, CEA, 38000 Grenoble, France

e-mail : emmanouil.giannoudis@cea.fr

Energy is the most important tool of modern communities in order to facilitate their daily life. Unfortunately, the modern energy economy is reliant on fossil fuels that cause serious environmental problems due to their combustion that produces carbon dioxide. This fact along with their depletion because of their continuous use has forced the scientific community to find clean and abundant energy sources, like solar, geothermal, wind power. Hydrogen, a typical example of these fuels, offers an alternative to fossil fuels. Hydrogen production into dye-sensitized-photoelectrochemical cells has gained an increased attention by molecular chemists. A typical cell combines a photoanode where water oxidation takes places to supply with electrons and protons the photocathode[1] where hydrogen production occurs. Our group already reported the first dye-sensitized photocathode based on a noble-metal free covalent dye-catalyst dyad, active under fully aqueous solution.[2] Ruthenium tris-diimine dyes are also widely used sensitizers for both photoanode and photocathode applications due to their long-lived photoexcited state, strong visible absorption and chemical stability. The group also previously studied NiO photocathodes sensitized by different ruthenium tris diimine complexes and highlighted the role played by the number of anchoring groups and the presence of a methylene spacer. Here, the synthesis and characterization of a new dyad combining the cobalt diimine-dioxime hydrogen-evolving catalyst with a ruthenium tris-diimine photosensitizer bearing four methyl phosphonate anchoring groups will be described. This dyad was grafted onto NiO films (Scheme 1) and was shown to display promising H_2-evolving photoelectrochemical activity. These results open new horizons for the construction of more efficient dye-sensitized H_2-evolving photocathodes.



Scheme 1. NiO photocathode based on the new RuCo dyad.

[1]. a) V. Nikolaou, A. Charisiadis, G. Charalambidis, A.G. Coutsolelos, F. Odobel, *J. Mater. Chem. A* **2017**, *5*, 21077. b) E. Gibson *Chem. Soc. Rev.* **2017**, *46*, 6194.
[2]. N. Kaeffer, J. Massin, C. Lebrun, O. Renault, M. Chavarot-Kerlidou, and V. Artero, *J. Am. Chem. Soc.*, **2016**, *138*, 12308.
[3]. N. Queyriaux, R.A. Wahyuono, J. Fize, C. Gablin, M. Wächtler, E. Martinez, D. Léonard, B. Dietzek, V. Artero, M. Chavarot-Kerlidou, *J. Phys. Chem. C.*, **2017**, *121*, 5891.

Supramolecular host-guest recognition of Re_6 clusters with cyclodextrins : size-matching and chaotropic effect

Anton A. Ivanov,[a,b] Clément Falaise,[a] Mohamed Haouas,[a] Yuri V. Mironov,[b]
Emmanuel Cadot[a]

[a] Institut Lavoisier de Versailles, UMR 8180, UVSQ, Université Paris-Saclay, 78035 Versailles, France
[b] Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russian Federation
e-mail : ivanov338@niic.nsc.ru

Octahedral rhenium cluster complexes due to their photoluminescent, redox and X-ray contrast properties are very promising for application in different fields of human life – medicine, biology, functional materials etc. On the other hand, cyclodextrins – cyclic oligosaccharide formed of 6, 7 or 8 glucopyranose units, are well known in medicine as a capsule for medical drugs. Such combination of clusters and CDs should improve the biocompatibility increasing potentialities of their applications. Also, we shown recently, that structurally close to cluster compound – polyoxometalates (POMs) can be used to obtain inclusion compounds with γ-cyclodextrin [1,2] to extend further POMs applications.

In this work, we studied the interactions in the system cyano rhenium clusters $[\{Re_6Q_8\}(CN)_6]^{4-}$ (Q = S, Se, Te) and cyclodextrins (α, β, or γ) by a set physicochemical methods in solution (multinuclear NMR spectroscopy, UV-vis, Mass spectrometry, ITC) and solid state (Single-crystal X-ray analysis) as well as influence of CD on the photophysical and redox properties (Fig. 1). This study reveals that inclusion compounds exist both in solution and solid state and strength of interaction depends on either size of cyclodextrin or on nature of the inner ligand of cluster. The main force in all combinations is size-matching as well as the physical-properties of the cluster-solvent interfaces, named chaotropic effect, which plays a preponderant role [3]. This knowledge will help us in future to design new biocompatible hybrid materials for biomedical applications.

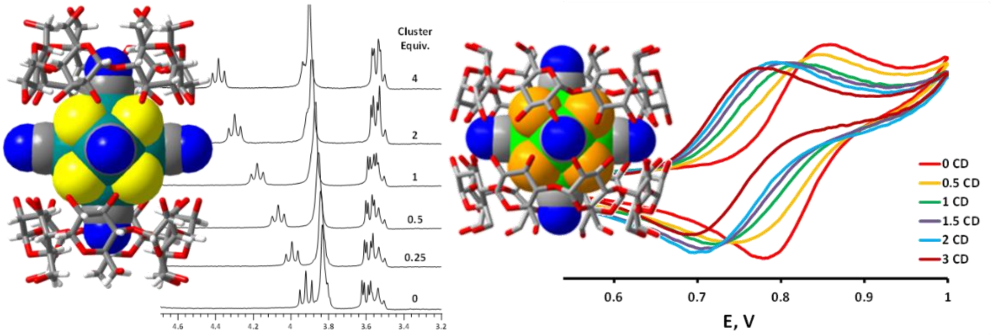


Figure 1. Fragment of crystal structure of $\{[\{Re_6S_8\}(CN)_6]\square 2\ \alpha\text{-CD}\}^{4-}$ (left) and $\{[\{Re_6Se_8\}(CN)_6]\square 2\gamma\text{-CD}\}^{4-}$ (right) and influence of cluster on ^1H NMR of CD (left) and CD on CV of cluster (right).

[1] M. Moussawi et al. *J. Am. Chem. Soc*. **2017**, 1*39*, 12793−12803
[2] C. Falaise et al. *J. Am. Chem. Soc*. **2018**, 1*40*, 11198−11201
[3] A. A. Ivanov et al. *Chem. Eur. J.* **2018**, *24*, 13467-13478

Cages auto-assemblées riches en électrons : contrôle redox de transformations supramoléculaires

Sébastien Goeb, Vincent Croué, György Szalóki, Serhii Krykun, Marc Sallé

[a] Laboratoire MOLTECH-Anjou, Université d'Angers, 2 bd Lavoisier, 49045 Angers Cedex
e-mail : sebastien.goeb@univ-angers.fr

La construction d'auto-assemblages discrets dont la synthèse est dirigée par les métaux connait un intérêt croissant depuis deux décennies. Leur structure, bi- ou tri-dimensionnelle, permet des applications dans divers domaines tels que la chimie hôte-invité, la catalyse en milieu confiné ou encore la vectorisation.[1] Contrôler leurs propriétés sous l'action d'un stimulus extérieur constitue aujourd'hui un défi important que de nombreuses équipes tentent de relever.[2]

Dans ce contexte, nous avons synthétisé les premiers édifices auto-assemblés à parois riches en électrons.[3] D'abord élaborés autour de ligands à base bis(pyrrolo)TTF (TTF : tétrathiafulvalène), ils ont permis la reconnaissance du fullerène C_{60},[4] et du TCNQ-F_4.[5] En s'appuyant ensuite sur un motif TTF-étendu (exTTF, Figure 1a), la seconde génération nous a permis d'accéder à une large gamme de structures 3D auto-assemblées capables de répondre à un stimulus redox. Dans cette communication, nous présenterons la préparation de cages de coordinations électro-actives (Figure 1b, c) en se focalisant sur leur capacité *i)* à encapsuler/relarguer réversiblement un invité[6] et *ii)* à opérer des transformations supramoléculaires.[7]

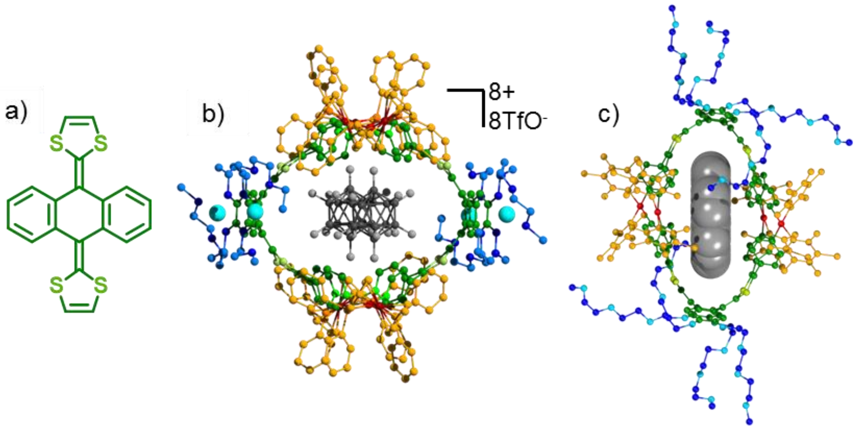


Figure 1. a) exTTF, b) Structure RX d'un complexe hôte-invité d'une cage auto-assemblée polycationique à base exTTF et c) Structure RX d'un complexe hôte-invité d'une cage auto-assemblée neutre à base exTTF.

[1]. T. R. Cook, et al., *Chem. Rev.*, **2015**, *115*, 7001.
[2]. a) W. Wang, et al., *Chem. Soc. Rev.*, **2016**, *45*, 2656. b) A. J. McConnell, et al., *Chem. Rev.*, **2015**, *115*, 7729.
[3]. V. Croué, et al., *Chem. Commun.*, **2015**, *51*, 7275.
[4]. S. Goeb, et al., *Chem. Commun.*, **2012**, *48*, 3106.
[5]. S. Bivaud, et al., *J. Am. Chem. Soc.*, **2013**, *135*, 10018.
[6]. a) V. Croué, et al., *Angew. Chem. Int. Ed.*, **2016**, *55*, 1746. b) 1. G. Szalóki, et al., *Angew. Chem. Int. Ed.*, **2017**, *56*, 16272.
[7]. G. Szaloki, et al., *Chem. Eur. J.*, **2018**, *24*, 11273.

Exploring versatile catalytic activity of stable porphyrin based MOFs

Alexandra Fateeva,[a] Jean-Bernard Tommasino,[a] Gia Co Quan, [a] Brian Abeykoon, [a]
Thomas Devic,[b] Alexander Sorokin,[c] Aude Demessence,[c]
Fréderic Maillard.[d]

[a] Université Claude Bernard Lyon 1, Laboratoire des Multimatériaux et Interfaces UMR 5615, F-69622 Villeurbanne, France
[b] Institut des Matériaux de Nantes,UMR 6502, 2 rue de la Houssinière, BP32229, 44322 Nantes, France
[c] Univ Lyon, Université Claude Bernard Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON, 2, avenue Albert Einstein, 69626 Villeurbanne, France
[d] Univ Grenoble Alpes, LEPMI, UMR 5279, F-38000 Grenoble, France, CNRS LEPMI, F-38000 Grenoble, France

Porphyrins are ubiquitous in enzymatic systems performing essential life processes such as catalytic aerobic oxidations, reduction and transport of O_2 etc[1]. Their high efficiency has stimulated extensive research devoted to the development of bio-inspired catalysts based on porphyrin scaffolds. In particular, porphyrin based metal organic frameworks (MOFs) provide interesting potential for heterogeneous catalysis when considering a precise structuration of catalytic sites in a porous network[2].
A series of stable porous porphyrinic frameworks were synthesised and structurally and spectroscopically characterised. The versatility of porphyrin chemistry allowed to access isotopic structures with diverse metallic centres inside the porphyrin core therefore leading to diverse functionalities. These materials were studied in a series of catalytic applications such as photocatalysis[3], electrocatalysis[4] and carbene transfer reactions[5]. Throughout our studies we aimed to understand the structure/activity relationship for these functional materials.

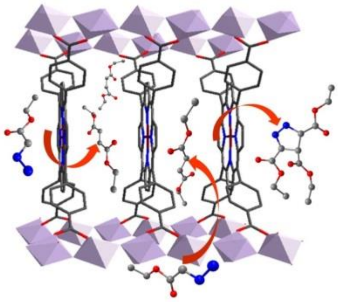


Figure 1. Porphyrin-based MOF displaying unusual activity for pyrazoline formation from ethyl diazoacetate[5]

[1] S. Ferguson-Miller and G. T. Babcock, *Chem. Rev.*, **1996**, *96*, 2889-2908
[2] W.-Y. Gao, M. Chrzanowski and S. Ma, *Chemical Society Reviews*, **2014**, *43*, 5841-5866.
[3]A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angewandte Chemie International Edition*, **2012**, *51*, 7440-7444.
[4] M. Lions, J. B. Tommasino, R. Chattot, B. Abeykoon, N. Guillou, T. Devic, A. Demessence, L. Cardenas, F. Maillard and A. Fateeva, *Chemical Communications*, **2017**, *53*, 6496-6499.
[5] B. Abeykoon, T. Devic, J.-M. Grenèche, A. Fateeva and A. B. Sorokin, *Chemical Communications*, **2018**, *54*, 10308-10311.

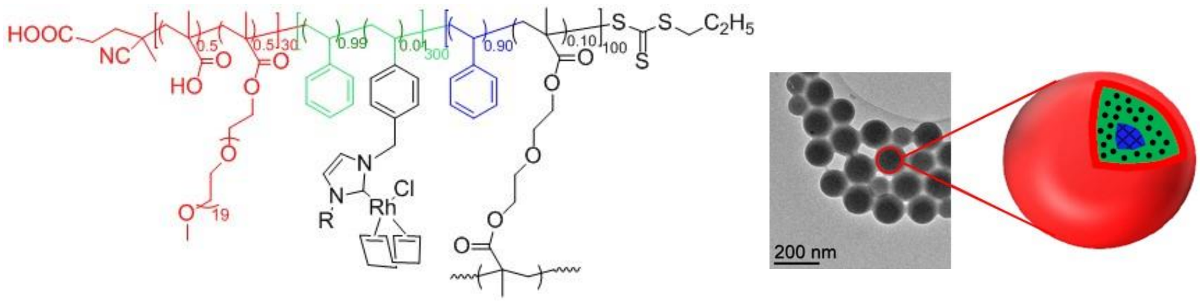
Hydrosoluble Polymeric Nanoreactors Containing Rh(I)-NHC Complexes for Biphasic Catalysis

Sasaline Salomon Sambou,[a] Audrey Allandrieu,[a] Eric Manoury, [a] Rinaldo Poli, [a,b] Agnès Labande [a] and Florence Gayet.[a]

[a] LCC-CNRS, Université de Toulouse, CNRS, INPT, Toulouse, France. [b] Institut Universitaire de France, 1, rue Descartes, 75231 Paris, France.
e-mail : agnes.labande@lcc-toulouse.fr

The recovery and recycling of catalysts have become essential prerequisites, for industrial applications, to improve energetic efficiency, limit the environmental footprint and lower the cost, especially when rare metals and expensive ligands are involved.

The use of polymeric structures with controlled architecture as catalytic supports is an emerging area. Our group has been interested for some time in the synthesis of unimolecular nanoreactors, called core-cross-linked micelles (CCMs), obtained by cross-linking of linear amphiphilic polymers after their self-assembly as micelles.[1] The main advantages of these objects compared to classical micelles is the absence of an equilibrium with free amphiphilic noncross-linked arms, leading to lower polymer and catalyst losses.



We have developed CCMs that incorporate rhodium(I) complexes bearing monodentate N-heterocyclic carbene ligands.[2] The complexes have been covalently bound to the polymeric chains by incorporation of a polymerizable unit on the NHC ligand. The substituent on the NHC has been changed in order to study its influence on the properties of the CCMs and on their activity in catalysis. The CCMs have been characterized by Dynamic Light Scattering and Transition Electron Microscopy, and evaluated as nanocatalysts for the hydrogenation of styrene under biphasic conditions.

[1] (a) X. Zhang, A.F. Cardozo, S. Chen, W. Zhang, C. Julcour, M. Lansalot, J.F. Blanco, F. Gayet, H. Delmas, B. Charleux, *Chem. – Eur. J.* **2014**, *20*, 15505-15517 ; (b) E. Lobry, A. Cardozo, L. Barthe, J.F. Blanco, H. Delmas, S. Chen, F. Gayet, X. Zhang, M. Lansalot, F. d'Agosto, R. Poli, E. Manoury, C. Julcour, *J. Catal.* **2016**, *164*, 172 ; (c) A. Joumaa, S. Chen, S. Vincendeau, F. Gayet, R. Poli, E. Manoury, *Mol. Catal.* **2017**, *438*, 267-271.
[2] Unpublished results.

Synthesis of complex or hybrid plasmonic nanostructures from organometallic precursors through ligand- or surface-controlled protocols

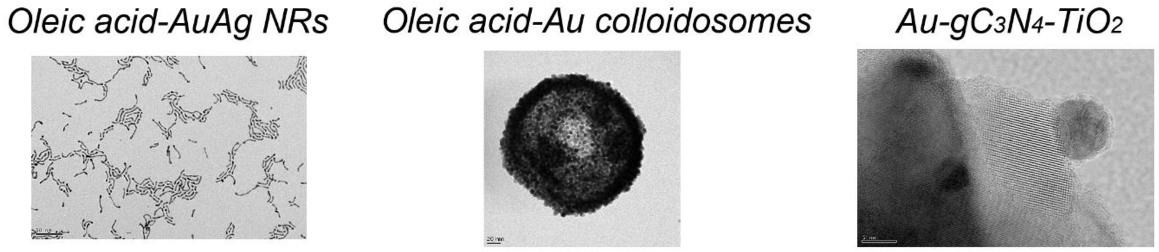
Miguel Monge,[a] Julian Crespo,[a] Marta Jiménez-Salcedo,[a] José M. López-de-Luzuriaga,[a] M. Elena Olmos,[a] Javier Quintana,[a] María Rodríguez-Castillo,[a] M. Teresa Tena[a]

[a] Departamento de Química. Centro de Investigación en Síntesis Química (CISQ). Universidad de La Rioja. Complejo Científico Tecnológico, Madre de Dios 51, 26006 - Logroño (LA RIOJA) - Spain.
e-mail : miguel.monge@unirioja.es

The control of the main characteristics of nanostructures is a prerequisite for an in-depth study of their properties, which change with size, shape, composition and surface state. At this regard, advanced synthetic protocols have shown that the combination of organometallic precursors with *in situ* changes in their coordination environments by addition of ligands has permitted to achieve a plethora of well controlled metal nanostructures.[1]

In this communication we show how the control of the reactivity of Au(I) or Au(I)-Ag(I) organometallic precursors such as $[Au(C_6F_5)(tht)]$ or $[Au_2Ag_2(C_6F_5)_4(Et_2O)_2]_n$ in the presence of oleic acid as ligand permits the controlled synthesis of new plasmonic gold or gold-silver complex nanostructures.[2] The precise control of the intermediates formed allows the synthesis of AuAg nanorods (NRs) or nanowires (NWs) (see Figure 1, left) or Au colloidosomes (see Figure 1, center), all of them displaying surface plasmon resonance absorptions in the NIR region.

We have also explored the *in situ* surface coordination chemistry of the bimetallic Au(I)-Ag(I) precursor $[Au_2Ag_2(C_6F_5)_4(Et_2O)_2]_n$ to graphitic carbon nitride (g-C_3N_4) 2D surfaces that serves as an interesting precursor for the design of visible-light active photocatalysts based on small size spherical AuAg nanoparticles deposited at the surface of g-C_3N_4 (see Figure 1, right).



Oleic acid-AuAg NRs *Oleic acid-Au colloidosomes* *Au-gC_3N_4-TiO_2*

Figure 1. Different metal nanostructures obtained by controlling the in situ addition of oleic acid to the organometallic precursors or through the coordination to a g-C_3N_4 surface.

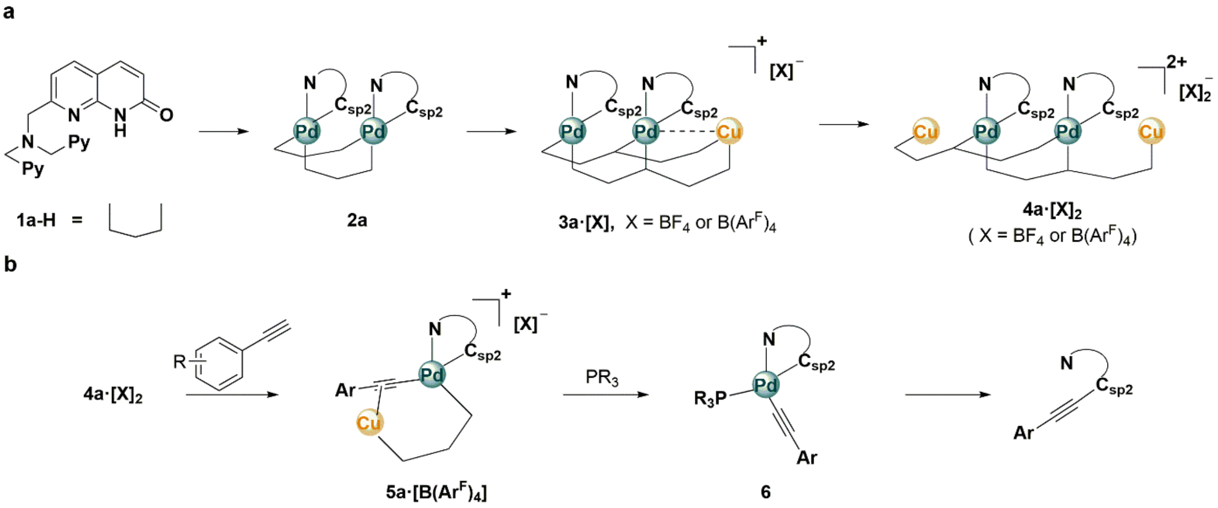
[1] C. Amiens, B. Chaudret, D. Ciuculescu-Pradines, V. Collière, K. Fajerwerg, P. Fau, M. Kahn, A. Maissonat, K. Soulantica, K. Philippot, *New J. Chem.* **2013**, *37*, 3374-3401.
[2] J. Crespo, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, M. Rodríguez-Castillo, B. Cormary, K. Soulantica, M. Sestu, A. Falqui, *Chem. Commun.* **2015**, *51*, 16691-16694.

timetallic Cu^{I}-Pd^{II} Linear Chain Complexes. Molecular Models for Sonogashira Coupling Reactions

Orestes Rivada-Wheelaghan,[a, b] Julia K. Khusnutdinova [a]

[a] Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University (OIST), Okinawa, Japan
[b] Laboratoire d'Electrochimie Moléculaire, UMR CNRS - P7 7591, Université Paris Diderot - Paris 7
e-mail : orestes.rivada@gmail.com

The cross-coupling reaction that involves a Pd^0-Cu^I catalytic system and forms a C-C bond between a terminal sp-hybridized carbon of a terminal alkyne with an sp^2 carbon of an aryl or a vinyl halide is commonly referred to as Sonogashira coupling.[1] Its general mechanism involves 3 steps: oxidative addition, transmetalation and reductive elimination. Despite the vast numbers of studies, fundamental understanding of the transmetalation step remains far from being well understood. Due to expected metal-metal cooperative effect during the transmetalation step, we have developed a set of linear chain Cu^I-Pd^{II} aryl complexes and studied their reactivity towards aryl acetylenes. The dynamic, unsymmetrical naphthyridinone-based ligand scaffolds, **1a-H** and **1b-H**,[2] have allowed us to synthesize and characterize a series of di-, tri- and tetranuclear species, due the "sliding" movement of the highly dynamic naphthyridinone frameworks (Scheme 1a). Moreover, these linear Cu^I-Pd^{II} multimetallic chain complexes are the first molecular models that undergo selective C_{sp2}-C_{sp} coupling product (Scheme 1b).[3] During our studies, we have isolated and characterized several intermediates in solution and solid state that are involved in Sonogashira coupling reaction.



Scheme 1. a, Development of linear chain multimetallic complexes containing ligand **1a-H**; **b**, Sonogashira coupling reaction promoted by multimetallic chain complex **4a·X$_2$**.

[1]. R. Chinchilla, C. Najera, *Chem Soc Rev* **2011**, *40*, 5084-5121.
[2]. O. Rivada-Wheelaghan, S. L. Aristizábal, J. López-Serrano, R. R. Fayzullin, J. R. Khusnutdinova, *Angew. Chem. Int. Ed.* **2017**, *51*, 16267-16271.
[3] a) I. Mena, P. Espinet, A. C. Albéniz, *Organometallics* **2014**, *33*, 1-7; b) R. J. Oeschger, P. Chen, *J. Am. Chem. Soc.* **2017**, *139*, 1069-1072.

Communications
par Affiches

EASY ACCESS TO CHELATING NHC-PHOSPHONIUM YLIDE COMPLEXES

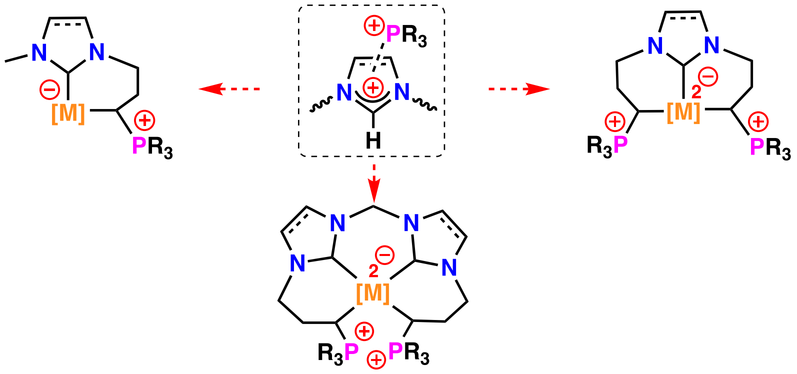
Rachid Taakili, Idir Benaissa, Cécile Barthes, Christian Bijani, Carine Duhayon, Christine Lepetit, Dmitry A. Valyaev, Noël Lugan, Yves Canac*

LCC-CNRS, Université de Toulouse, 205 route de Narbonne 31077 Toulouse, France
e-mail: yves.canac@lcc-toulouse.fr

Following the report of the first stable N-heterocyclic carbene (NHC),[1] the functionalization of these species became a major issue because of their many applications in the field of organometallic chemistry, homogeneous catalysis and materials.[2] The introduction of a phosphine onto the heterocycle led to the development of a large variety of heteroleptic systems, whose intrinsic properties appear closely related to their relative position.[3] The phosphorus moiety can formally replace or cooperate with the carbenic center, depending on whether it is directly attached to the latter or located at the other positions of the heterocycle. This association leads respectively to the formation of an electron-poor imidazoliophosphine or to a phosphorylated imidazolium salt.[3,4]

The phosphorus group can also be introduced on the NHC moiety as a phosphonium.[4] By analogy with cationic phosphines, the presence of a positive charge on the NHC, regardless of its position, is expected to modulate the physico-chemical properties of the system. If the charge is located near the carbenic center, it can also influence the electronic properties and a decrease in the donating character of the NHC is then observed. Another advantage of the charge is the ease of converting the phosphonium group into the corresponding ylide by a deprotonation reaction.[4]

This latter reactivity is used here to prepare new chelating NHC-phosphonium ylide complexes in the bi-,[5] tri-[6] and tetradente[7] series from easily accessible NHC pre-ligands bearing one or more phosphonium fragments. These complexes should benefit catalytic processes requiring electron-rich ligands.



[1] A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc*. **1991**, *113*, 361–363.
[2] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485–496.
[3] S. Gaillard, J. L. Renaud, *Dalton Trans*. **2013**, *42*, 7255–7270.
[4] Y. Canac, *Chem. Asian. J.* **2018**, *13*, 1872–1887.
[5] I. Benaissa, R. Taakili, N. Lugan, Y. Canac, *Dalton Trans*. **2017**, *46,* 12293–12305.
[6] R. Taakili, Y. Canac, and *coll*. *Unpublished results*.
[7] C. Barthes, C. Bijani, N. Lugan, Y. Canac, *Organometallics* **2018**, 37, 673–678.

Unveiling the redox-active character of amino-substituted N-heterocyclic carbenes

Mirko Ruamps,[a] Stéphanie Bastin,[a] Lionel Rechignat,[a] Dmitry A. Valyaev,[a] Yin Zhang,[a] Jean-Marie Mouesca,[b] Noël Lugan,[a] Vincent Maurel,[b] Vincent César[a]

[a] LCC-CNRS, 205 route de Narbonne, 31077, Toulouse cedex 4, France
[b] Université Grenoble Alpes, CEA, CNRS, INAC, SyMMES, F-38000 Grenoble, France
e-mail: vincent.cesar@lcc-toulouse.fr

Redox non-innocent ligands have gained considerable significance in homogeneous catalysis, due to their ability to act as electron reservoirs across the catalytic cycle.[1] However, even if N-Heterocyclic Carbenes (NHCs) were shown to feature such a property,[2] only few examples of redox-active NHCs exist in literature.[3]

Continuing our research effort on backbone functionalized NHCs, we disclosed in 2014 a new type of NHCs with improved catalytic efficiency, namely the 4-(amino)imidazol-2-ylidene IAr$^{(\mathrm{NR_2})}$ and especially the 4,5-bis(dimethylamino)imidazol-2-ylidene IAr$^{(\mathrm{NMe_2})_2}$.[4] We now present our progress towards the assessment of the redox properties of these NHCs.

A complete study was carried out on the archetypal 1,3-dimesityl-4-(dimethylamino)imidazol-2-ylidene [IMes$^{\mathrm{NMe_2}}$] and 4,5-(bis(dimethylamino)imidazol-2-ylidene, [IMes$^{(\mathrm{NMe_2})_2}$]. Several organic compounds as well as transition-metal complexes based on these NHCs were synthesized and characterized and their redox properties were thoroughly evaluated by electrochemistry and EPR spectroscopy, complemented by DFT calculations.[5]

[1] P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794-795.
[2] D. Rottschäfer, B. Neumann, H. G. Stammler, M. v. Gastel, D. M. Andrada, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2018**, *57*, 4765-4768 and references therein.
[3] E. Peris, *Chem. Rev.* **2018**, *118*, 9988-10031.
[4] (a) Y. Zhang, G. Lavigne, N. Lugan, V. César, *Chem. Eur. J.* **2017**, *23*, 13792-13801; (b) V. César, Y. Zhang, W. Kośnik, A. Zieliński, A. A. Rajkiewicz, M. Ruamps, S. Bastin, N. Lugan, G. Lavigne, K. Grela, *Chem. Eur. J.* **2017**, *23*, 1950-1955; (c) Y. Zhang, G. Lavigne, V. César, *J. Org. Chem.* **2015**, *80*, 7666-7673; (d) Y. Zhang, V. César, G. Lavigne, *Eur. J. Org. Chem.* **2015**, *2015*, 2042-2050; (e) Y. Zhang, V. César, G. Storch, N. Lugan, G. Lavigne, *Angew. Chem. Int. Ed.* **2014**, *53*, 6482-6486.
[5] M. Ruamps, S. Bastin, L. Rechignat, A. Sournia-Saquet, D. A. Valyaev, J.-M. Mouesca, N. Lugan, V. Maurel, V. César, *Chem. Commun.* **2018**, *54*, 7653-7656.

Homogeneous Catalytic Hydroboration of Carbon Dioxide

Dan Zhang,[a] Sébastien Bontemps.[a]

[a] *LCC CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 4*
e-mail : dan.zhang@lcc-toulouse.fr

As a nontoxic and sustainable carbon source, carbon dioxide has attracted increasing attention over the last few decades. Significant efforts have been devoted to the transformation of CO_2 and especially its reduction under mild conditions. However the selective reduction of CO_2 to the formaldehyde level is still a challenge.[1]
Very few examples of selective hydroboration of CO_2 into bis(boryl)acetal (BBA) have been described to date.[2-5]
We thus aimed at probing first row metal hydride catalysts (M= Fe, Co, Mn) and non-commercially available hydroboranes to enlarge the scope of accessible BBA (Figure 1). We will present these results and the impact of the boryl moiety on the reactivity of these compounds.

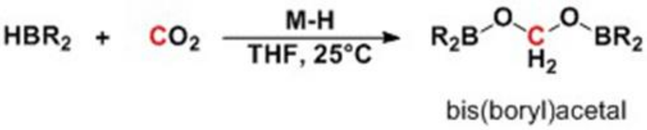


Figure 1. CO_2 hydroboration

[1]. S. Bontemps, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.*, **2014**, *136*, 4419-4425.
[2]. G. Jin, C. G. Werncke, S. Bontemps, *J. Am. Chem. Soc.*, **2015**, *137*, 9563-9566.
[3]. C. D. N. Gomes, E. Blondiaux, P. Thuéry, T Cantat, *Chem. Eur. J.*, **2014**, *20*, 7098–7106.
[4]. L. J. Murphy, H. Hollenhorst, R. McDonald, M. Ferguson, M. D. Lumsden, L. Turculet, *Organometallics*, **2017**, *36*, 3709-3720.
[5]. M. Courtemanche, A. P. Pulis, E. Rochette, M. Légaré, D. W. Stephan, F. Fontaine, *Chem. Commun.,* **2015**, *51*, 9797-9800.

Perhalophenyl Gold(I) complexes and their fascinating photophysics: luminescent solvatochromism and TADF examples

María Rodríguez-Castillo,[a] José María López-de-Luzuriaga,[a] Miguel Monge,[a] M. Elena Olmos,[a] Javier Quintana,[a] Inés Soldevilla[a]

[a] Departamento de Química. Centro de Investigación en Síntesis Química (CISQ). Universidad de La Rioja. Complejo Científico Tecnológico, Madre de Dios 51, 26006 - Logroño (LA RIOJA) - Spain.
e-mail : maria.rodriguez@unirioja.es

One of the most interesting properties that perhalophenyl gold(I) complexes show is their luminescent behaviour. Its origin has different possibilities such as: i) the presence of Au(I)···M (M = closed shell metal) metallophillic interactions or ii) the geometry of the gold centre, among others. In this communication, examples of both situations are represented:
It is well-known the tendency of Au(I) centres to generate metallophilic interactions with a large number of closed-shell metals,[1] especially the ones from group 11. In this sense, an acid-base reaction between bisperhalophenylaurate units and silver salts has been very productive in order to obtain heterometallic gold(I) complexes displaying, at the same time, unsupported Au(I)···Ag(I) and Au(I)···Au(I) interactions. Using these compounds as starting material and pyridazine as ligand, it is possible to obtain stimuli-responsive heterometallic Au(I)-Ag(I) clusters based on its reversible solvatochromism luminescence behaviour induced by the nature of the solvent.
On the other hand, tricoordinated Au(I) complexes represent another possibility to obtain luminescent complexes through the simple control of the coordination environment of gold.[2] In addition, we have observed that structurally rigid perhalophenyl gold(I) complexes coordinated to chelating diphosphine ligands display Thermally Activated Delayed Fluorescence (TADF). The photophysical properties of the synthesized complexes have been studied in depth.

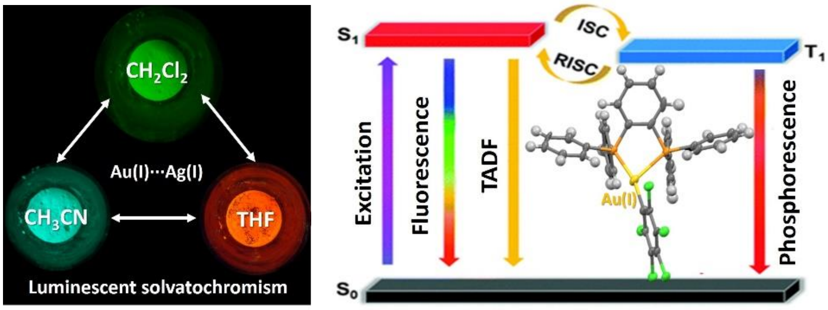


Figure 1. Luminescent solvatochromism based on metallophilic interactions (left) and tricoordinated Au(I) complex displaying TADF (right).

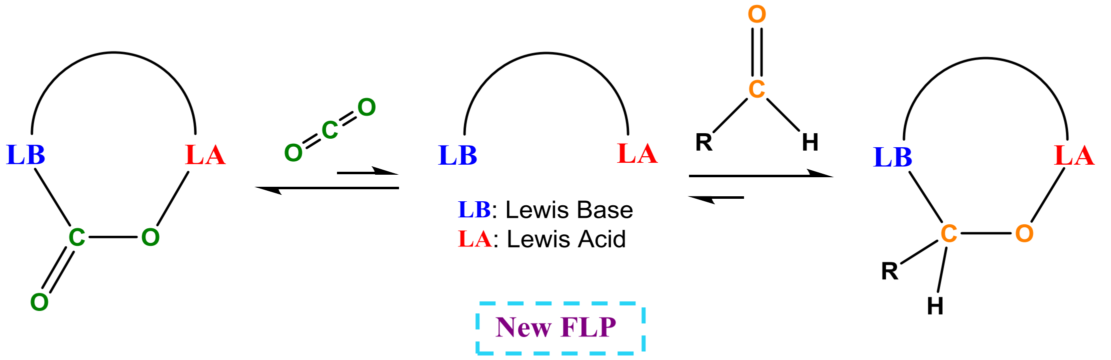
[1] V.W. Yam, V. K.-M. Au, S. Y.-L. Leung, *Chem.Rev.* **2015**, *115*, 7589-7728.
[2] M. Osawa, M. Aino, T. Nagakura, M. Hoshino, Y. Tanaka, M. Akita, *Dalton Trans.* **2018**, *47*, 8229-8239.

New unstable Frustrated Lewis Pair for the activation of aldehydes

Angelica Mejia Fajardo,[a] Sébastien Bontemps.[a]

[a] *CNRS, LCC 205 route de Narbonne BP 44099, F-31077 Toulouse cedex 4, France.*
e-mail: angelica.mejia@lcc-toulouse.fr

Frustrated Lewis Pair (FLP) has been an important field of main-group chemistry since the seminal report of D. W. Stephan in 2006.[1] This kind of system is composed of a Lewis base and a Lewis acid which cannot form a Lewis pair, due to geometry or steric hindrance.[2] This unique feature gives rise to interesting reactivities involving small molecules and carbon dioxide in particular.[3] The present work describes a new FLP system. Although it could not be isolated nor observed, it was transiently generated and stabilized by the trapping of a CO_2 molecule. Moreover, the CO_2 adduct was used as a masked form of this unstable FLP to activate aldehydes. We studied the different reactions involved in order to understand the current mechanism.



CO_2 activation
Masked form of FLP

Not observed
Not isolated

Aldehyde activation
Characterized

[1]. G. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, 314, 1124-1126.
[2]. D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, 54, 6400-6441.
[3]. S. Bontemps, *Coord. Chem. Rev.* **2016**, *308*, 117-130.

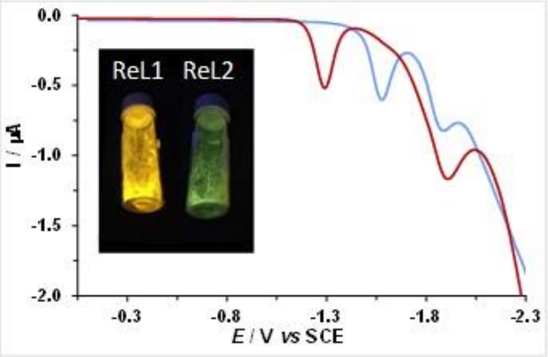
Electrochemical and Luminescence Properties of Two Rhenium Complexes: the Unsuspected Influence of the Pyridyl-Triazole Ligand Isomerism

Béatrice Delavaux-Nicot,[a,b] Jinhui Wang,[c] Alain Moreau,[a,b] Eric Benoist,[c] Suzanne Fery-Forgues[c]

[a] Laboratoire de Chimie de Coordination, CNRS – UPR 8241, 205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4, France. [b] Université de Toulouse UPS, INPT 31077 Toulouse Cedex 4, France. [c]SPCMIB, CNRS UMR 5068, Université Toulouse III Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 9
e-mail : beatrice.delavaux-nicot@lcc-toulouse.fr

Two tricarbonyl rhenium(I) complexes, **ReL1** and **ReL2**, that only differ by the nature of their 2-pyridyl-1,2,n-triazole (pyta) ligand (with n = 4 and 3, respectively) connected to a 2-phenylbenzoxazole (PBO) moiety, have been synthesized in good yields. The X-ray structures indicate that in **ReL1** the PBO moiety and the pyta ligand almost form a right angle hindering electron delocalization, while in **ReL2** their nearly planar arrangement favors the electron delocalization in the whole organic ligand. Surprisingly, **ReL2** emits at shorter wavelengths than **ReL1**. Remarkably, these compounds also emit in the solid state, but only **ReL1** exhibits a significant aggregation-induced phosphorescence emission (AIPE). Electrochemistry is a method of choice to clearly visualize and better understand some key factors of this study. Moreover, the provided data are in perfect agreement with theoretical calculations and optical properties.

This complete study sheds light on the crucial role of structural isomerism of the triazole group, which has been unsuspected for a long time although it can govern the geometry and electronic properties of rhenium complexes. For the first time, it is evidenced that grafting a non-coordinated π-conjugated fragment on the N(4) atom of a 1,2,4-triazole group can be of high value for the design of efficient light-emitting materials based on rhenium complexes.[1]



OSWVs: cathodic scans of complexes **ReL1** (red) and **ReL2** (blue) on a Pt working electrode in CH_2Cl_2 + 0.1 M *n*[Bu_4N][BF_4] at room temperature. Photo: luminescence in the solid state upon illumination by a UV lamp (365 nm).

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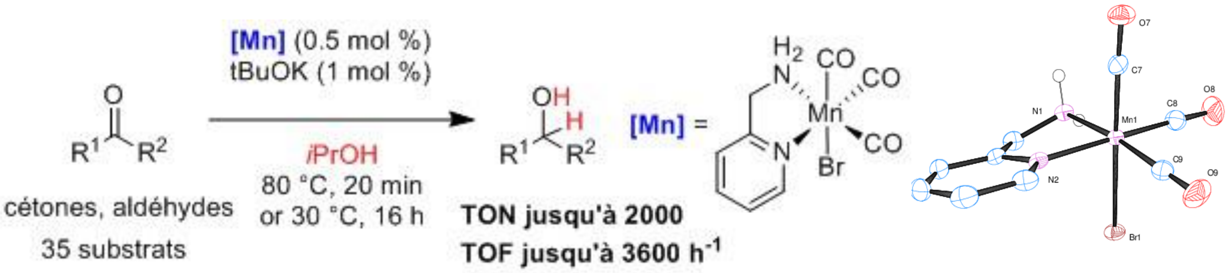
[1]. J. Wang, B. Delavaux-Nicot, M. Wolff, S. Mallet-Ladeira, R. Métivier, E. Benoist, S. Fery-Forgues, *Dalton Trans.* **2018,** *47*, 8087- 8099.

Réduction de Dérivés Carbonylés Catalysée par des Pré-catalyseurs Bon-marchés à Base de Manganèse

Antoine Bruneau-Voisine,[a,b] Ding Wang,[a] Jean-Baptiste Sortais[b]

[a] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, 263 av. du General Leclerc, 35042 Rennes Cedex, France.
[b] LCC–CNRS, Université de Toulouse, UPS, 205 route de Narbonne 31077 Toulouse Cedex 4, France.
e-mail : jean-baptiste.sortais@lcc-toulouse.fr

Le développement de systèmes catalytiques basés sur des métaux non-nobles a connu une forte progression depuis dix ans.[1] Dans le cas du manganèse, qui est le troisième métal de transition le plus abondant après le fer et le titane, la réduction de liaisons C=O était, jusque récemment, limité à l'hydrosilylation et l'hydroboration de dérivés carbonylés ainsi qu'à la réduction électrochimique du CO_2.[2] Depuis 2 ans le domaine de l'hydrogénation avec des complexes de Mn^I a connu une forte expansion, depuis le travail pionnier de Beller et *coll.*,[3] notamment avec l'utilisation de ligands tridentate de type PNP. Les principaux défauts de ce type de ligand sont leur complexité de synthèse et leur prix qui atténuent le fait d'utiliser un métal bon-marché.



Dans ce travail nous avons développé un système catalytique basé sur l'utilisation de manganèse comme métal abondant associé à un ligand bidenté très simple, la 2-methylaminopyridine, pour la réduction de cétones et d'aldéhydes en utilisant l'isopropanol comme source d'hydrogène.[4] Remarquablement, cette réaction fonctionne à température ambiante ainsi qu'avec de basses charges catalytique (jusqu'à 0,1 mol%) et tolère une grande diversité de groupements fonctionnels.

[1]. G.A. Filonenko, R. van Putten, E.J.M. Hensen, E.A. Pidko, *Chem. Soc. Rev.*, **2018**, *47*, 1459; F. Kallmeier, R. Kempe, *Angew.*, **2018**, 57, 1, 46.
[2]. Valyaev, D. A., Lavigne, G., Lugan, N., Coord. Chem. Rev., **2016**, 308, 191.
[3]. S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel, M. Beller, Nat. Commun., **2016**, 7, 12641.
[4]. A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, *Org. Lett.*, **2017**, *19*, 3656.

Modification de capteurs d'oxydes métalliques semi-conducteurs par des nanomembranes à base de MOFs

Drobek Martin,[a] Kim Jae-Hun,[b] Bechelany Mikhael,[a] Weber Matthieu,[a] Julbe Anne,[a] Kim Sang Sub.[b]

[a] Institut Européen des Membranes, France ,[b] Inha University, Republic of Korea
e-mail : martin.drobek@univ-montp2.fr

Les capteurs de gaz présentent un grand intérêt pour une large diversité d'applications nécessitant notamment la détection de gaz toxiques ou explosifs, la surveillance de la qualité de l'air, le diagnostic médical ou le contrôle des propriétés alimentaires/cosmétiques.
Récemment des nombreux d'effets de recherche ont été consacrés à l'amélioration des performances des capteurs à base d'oxydes métalliques semi-conducteurs (SMO) pour la détection de gaz.
Dans ce travail, nous avons mis au point une stratégie innovante pour améliorer la sélectivité des capteurs d'oxydes métalliques ZnO par recouvrement des nanofils de ZnO avec une nanomembrane de type tamis moléculaire à base de MOF. En comparaison avec les capteurs ZnO vierges, leurs homologues ZnO/MOF optimisés (e.g. ZnO/ZIF-8 ou ZnO/SIM-1) présentent une sélectivité remarquable vis-à-vis de H2 à des températures élevées (max. 300°C) en présence de gaz interférants, confirmant ainsi l'efficacité de ces capteurs pour la détection d'hydrogène [1,2]. Cette stratégie originale d'encapsulation avec des membranes MOF ouvre la voie à d'autres architectures 3D complexes à différents types d'applications nécessitant une sélectivité en gaz, molécules ou ions, notamment dans le domaine des biocapteurs, photo(catalyseurs) et électrodes.

[1] M. Drobek, J.H. Kim, M. Bechelany, C. Vallicari, E. Leroy, A. Julbe, S. S. Kim, Sensors and Actuators B 264 (2018) 410–418.
[2] M. Drobek, J.-H. Kim, M. Bechelany, C. Vallicari, A. Julbe, and S.S. Kim, MOF-Based Membrane Encapsulated ZnO Nanowires for Enhanced Gas Sensor Selectivity, ACS Applied Material & Interfaces 8 (2016) 8323–8328.

Silver Nanoparticles; Parametric study and modeling by application of the experimental design methodology

Houamria Hamza [a], Merah Abdelali [b], Bouledroua Samia

[a] *: (Faculty of Medicine, Department of pharmacy/Laboratory of Inorganic Chemistry, University of Badji Mokhtar Annaba/ALGERIA, Zaâfrania B.P 205, 23000, Annaba, Algeria).*
[b] *Adresse auteur n°2 : (Faculty of Medicine, Department of pharmacy/Laboratory of Inorganic Chemistry, University of Badji Mokhtar Annaba/ALGERIA, Zaâfrania B.P 205, 23000, Annaba, Algeria).*
e-mail : hamzapharm2000@yahoo.fr

Silver colloids, silver nanoparticles suspended in liquid exposure properties Chemical, optical and antimicrobial materials widely used in a wide field of application. For these antibacterial and antifungal and antiviral qualities, psoriasis and eczema, these Specific properties are heavily influenced by particle size and shape

The methodology of the experiments plans is an optimal strategy allowing to organize the tests which accompany. A scientific research allows it to obtain the maximum of information with a maximum of precision from a minimum number of experiments in the fastest time and for the least cost[1]

Our work consists in successfully synthesizing a colloidal solution of silver nanoparticles with the use of nitrate of silver as precursor and sodium citrate as reducing agent and optimizes the operating conditions

Materials and Methods: thermometer for solution, centrifuge, Analytical Balance, UV-spectrophotometer. [2]

Observations: It should be noted that the process of formation and growth of nanoparticles can be easily affected by a multitude of factors, all the glassware must be cleaned by a solution of aqua regia

Results: The field of study allows to synthesize colloids whose mean particle size varies between 59.22nm and 111.85nm.

Discussion: A change in the concentration of citrate in the colloid has an effect on the rate of reduction and on the nucleation / growth ratio. [3]

Conclusion: synthesis of a silver colloid by chemical reduction using silver nitrate as a precursor and sodium citrate is easy to achieve[4]

[1]. Anderson. A et al: press.sci comm. 2005. 27.200-220.
[2]. Arora. S et al : toxicol. Appl. Pharmacol. 2009. 236.310-318.
[3]. Asharani. P V et al: ACS NANO. 2009. 3,279-290.
[4] Burchardt. A et al: environ.sci.technol. 2012. 46, 11336-11344.

Investigating the antitumor properties of new $Mo_2O_2S_2$-based coordination compounds with thiosemicarbazones

A. Fuior,[a,b] S. Floquet,[a] A. Gulea,[b] M. Haouas,[a] C.Falaise,[a] J. Marrot,[a] E. Cadot.[a]

[a] *ILV, Université de Versailles - CNRS UMR 8180, Versailles, France,*
[b] *Moldova State University, 60 Alexei Mateevici str., MD-2009 Chișinău, Moldova*
E-mails: arcadie.fuior@uvsq.fr, sebastien.floquet@uvsq.fr

The cyclic polyoxothiomolybdate $K_{2-x}(NMe_4)_x[I_2Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5]x20H_2O$ acts as a source of dinuclear units $[Mo_2O_2S_2(H_2O)_6]^{2+}$ which can be involved in the formation of many types of spectacular (supra)molecular structures with various dimensions and architectures.[1,2] One surprising application found for such $[Mo_2O_2S_2(H_2O)_6]^{2+}$-based structures is their properties in different domains of biology such as biomass growing, beekeeping, or antioxidative properties.[3] The aim of this work is to get new coordination compounds based on $[Mo^{(V)}{}_2O_2S_2]^{2+}$ fragments with increased anticancer activity by using thiosemicarbazone ligands. Thiosemicarbazones (Thx) are widely recognised for their diverse range of biological activity, including anti-fungal, antibacterial and anti-cancer effects and it is also known that bonding them to cations of transition metals leads to molecules about 10 times more efficient.[4] Therefore this motivated us to synthesize $[Mo_2O_2S_2(Thx^-)_2]$ complexes and to explore their potential biological properties. Here we report a series of 12 new dinuclear $Mo^{(V)}$ coordination compounds with various thiosemicarbazone ligands R_1–$C(R_2)$=N–NH–C(S)–NH–R_3 (R_1= C_6H_5N(**1**), C_6H_4OH(**2**), $C_{10}H_6OH$(**3**), C_9H_6N(**4**), $C_7H_6(OH)_2N$(**5**), C_4H_3O(**6**), C_4H_3S(**7**); R_2=H(**1**,**2**,**3**,**4**,**5**,**6**,**7**), CH_3(**8**,**9**,**11**); R_3= H(**1**,**2**,**3**,**4**,**5**,**6**,**7**,**11**), CH_3(**10**,**12**), C_6H_{11}(**8**), $C_6H_4NHCOCH_3$(**9**).)

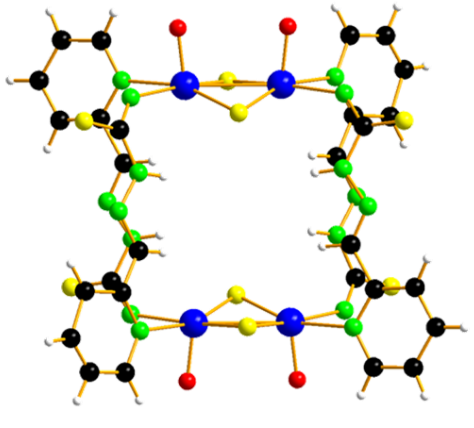


Fig. 1. Compound **1** $[(Mo_2O_2S_2)_2(Thpy)_4]$

Solid-state characterization, including X-ray Diffraction, allowed us to reveal novel and original structures for the compounds **1**, **3**, **4** and **9**, having unexpected coordination types (fig. 1). For our studies in solution we focused on multiple multinuclear NMR techniques (COSY, ROESY, DOSY, $^{13}C\{^1H\}$ HSQC, $^1H\{^{15}N\}$ HMBC) to support and confirm the agreement with previous analysis results. The obtained compounds were then tested on HeLa and BxPc3 cancer cells and we show that compounds possessing free –OH groups (**2** and **3**) have a stronger activity on BxPc3, with IC_{50} values corresponding to 3.5 μM and 5.67 μM respectively.

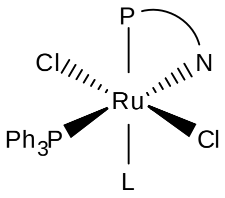
[1]. *E. Cadot, M.N. Sokolov, V.P. Fedin, C. Simonnet-Jégat, S. Floquet, F. Sécheresse, Chem. Soc. Rev.,* ***2012****, 7335-7353.*
[2]. *J.-F. Lemonnier, S. Duval, S. Floquet and E. Cadot. Isr. J. Chem.,* ***2011****, 51, 290-302.*
[3] *S. Floquet, E. Cadot, A. Hijazi, A. Gulea, V. Tapcov, V. Bulimaga, L. Zosim. Patent N° 4319 MD, MD - BOPI 1/****2015*** *p33; " I. Toderas, A. Gulea, V. Cebotari, S. Floquet, E. Cadot, I. Buzu. MD - BOPI 4/****2016*** *p16.*
[4] *E. Pahontu, V. Fala, A. Gulea, D. Poirier, V. Tapcov and T. Rosu / Molecules* ***2013****, 18, 8812-8836*

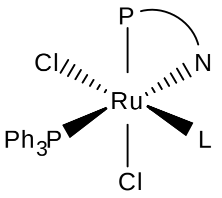
Interprétation Orbitalaire des Propriétés Magnétiques de Complexes Ru(II)

Eliott Norbert-Agaisse,[1] Christophe Raynaud,[1] Odile Eisenstein[1] .

1 Institut Charles Gerardt Montpellier, équipe CTMM, université de Montpellier
e-mail : eliott.norbert-agaisse@umontpellier.fr

La Résonance Magnétique Nucléaire est une technique de caractérisation incontournable en chimie. La corrélation charge/déplacement chimique, bien que suffisante pour l'analyse des spectres H^1 de molécules organiques, s'avère non transposable à d'autres noyaux ainsi qu'à la chimie inorganique. La théorie, par l'intermédiaire d'analyse de la structure électronique, donne l'opportunité de rationaliser des propriétés sondées par RMN telles que l'anisotropie du tenseur de blindage. La synthèse et caractérisation d'une famille de complexes de Ruthénium, se distinguant par la nature du ligand L (H_2, H_2S, H_2O, vacant, NO^+, N_2O, CO), a mis en évidence une corrélation déplacement chimique du phosphore P_1 avec la distance de ce dernier et du métal.





Nous avons alors cherché à apporter l'explication théorique à l'origine de ce comportement.
Notre approche consiste, dans en premier temps, à nous assurer de la capacité de nos méthodes théoriques (Fonctionnelle de la densité) à reproduire les valeurs expérimentales du déplacement chimique isotrope de ces complexes.
En second lieu, nous cherchons à décomposer le déplacement chimique en différentes contributions à l'aide d'une méthode de décomposition du blindage (Natural Chemical Shift).
Enfin nous pouvons associer ces contributions aux orbitales localisées obtenues à l'aide de l'approche NBO (Natural Bonding Orbital) et ainsi rationaliser le lien existant entre le déplacement chimique, la distance Ru-P et le champ de ligand.

Cu- and Fe-catalyzed oxidative amidation

X. Bantreil,[a] A. N. Bilyachenko,[b] E. S. Shubina,[b] E. Clot,[c] F. Lamaty[a]

[a] *Institut des Biomolécules Max Mousseron (IBMM) UMR 5247, CNRS, Université de Montpellier, ENSCM, Université de Montpellier Campus Triolet Place Eugène Bataillon 34095 Montpellier Cedex 5, France*
[b]*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str., 28, 119991 Moscow, Russia.*
[c]*Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM,*
Université de Montpellier, cc 1501, 34095 Montpellier Cedex 5, France
e-mail : frederic.lamaty@umontpellier.fr

The amide bond is of high importance in a wide number of natural and pharmaceutical products as well as polymers and materials. However, general methods to synthesize an amide involve an activated acid and amine, generating at least one equivalent of toxic waste from the coupling agent. In this context, we recently developed the direct benzamide formation from alcohols catalyzed by inexpensive copper and iron salts.[1,2,3] The amidation reaction could also be performed using down to 100-500 ppm of copper or iron when unprecedented copper or iron silsesquioxanes or germsesquioxanes complexes were used.[4,5,6]

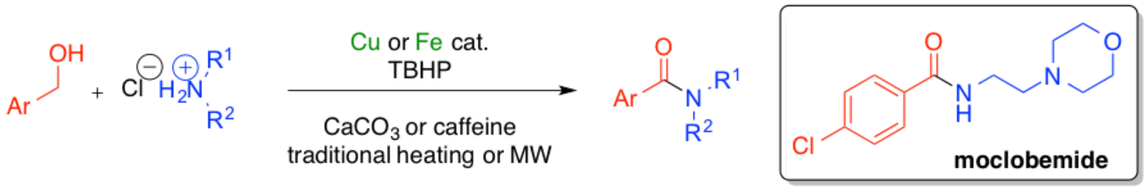


Figure 1 : Oxidative amidation for the synthesis of moclobemide

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[1] Bantreil, X.; Kanfar, N.; Géhin, N.; Golliard, E.; Martinez, J.; Lamaty F. *Tetrahedron* **2014**, *70*, 5093-5099.

[2] Bantreil, X.; Fleith, C.; Martinez, J.; Lamaty, F. *ChemCatChem* **2012**, *4*, 1922-1925.

[3] Bantreil, X.; Navals, P.; Martinez, J. Lamaty, F. *Eur. J. Org. Chem.* **2015**, 417-4224.

[4] Bilyachenko, A. N.; Dronova, M. S.; , Yalymov, A. I.; Lamaty, F.; Bantreil, X.; Martinez, J.; Bizet, C.; Shul'pina, L. S.; Korlyukov, A. A.; Arkhipov, D. E.; Levitsky, M. M.; Shubina, E. S.; Kirillov, A. M.; Shul'pin, G. B. *Chem. Eur. J.* **2015**, *21*, 8758-8770

[5] Bilyachenko, A. N.; Levitsky, M. M.; Yalymov, A. I.; Korlyukov, A. A.; Vologzhanina, A. V.; Kozlov, Y. N; Shul'pina, L. S.; Nesterov, D. S.; Pombeiro, A. J. L.; Lamaty, F.; Bantreil, X.; Fetre, A.; Liu, D.; Martinez, J.; Long, J.; Larionova, J.; Trigub, A. L.; Zubavichus, Y. V.; E. Golub, I. E.; Filippov, O. A.; Shubina, E. S.; Shul'pin, G. B.
RSC Adv. **2016**, *6*, 48165-48180

[6] Bilyachenko, A. N.; Levitsky, M. M.; Yalymov, A. I.; Korlyukov, A. A.; Khrustalev, V. N.; Vologzhanina, A. V.; Shul'pina, L. S.; Ikonnikov, N. S.; Trigub, A. L.; Dorovatovsky, P. V.; Bantreil, X.; Lamaty, F.; Long, J.; Larionova, J.; Golub, I. E.; Shubina, E. S.; Shul'pin, G. B. *Angew. Chem. Int. Ed.* **2016,** *81***,** 15360-15363

Mise en œuvre de MOF sous forme monolithique à partir d'émulsions de Pickering

Fabrice Lorignon[a,b]*, Marine Cognet[a], Alban Gossard[b], Michael Carboni[a], Daniel Meyer[a]

[a] *Institut de Chimie Séparative de Marcoule, UMR 5257, CEA/CNRS/ENSCM/UM,*
F-30207 Bagnols-sur-Cèze, France
[b] *CEA, DEN, DE2D, SEAD, Laboratoire des Procédés Supercritiques et de Décontamination,*
Marcoule, F-30207 Bagnols-sur-Cèze, France
E-mail : *fabrice.lorignon@cea.fr*

La montée industrielle, l'agriculture intensive ainsi que l'évolution démographique font de la pollution de l'environnement un des enjeux majeurs de notre siècle. Les milieux impactés sont l'air, les sols et les eaux et différents procédés de décontamination voient régulièrement le jour. En ce sens, la décontamination des eaux à l'aide de supports solides est aujourd'hui un procédé qui tend à se développer fortement dans les années à venir.

Les MOFs (Metal-Organic Frameworks) sont une nouvelle classe de matériaux poreux et apparaissent prometteurs pour ce mode de décontamination. Ces matériaux résultent de l'auto-assemblage d'un métal et d'un ligand organique. Ils sont étudiés et appréciés pour leur surface spécifique importante, leur taille de pores modulable, leurs propriétés contrôlables et leur stabilité chimique [1]. La littérature a montré que l'utilisation de MOFs pour l'extraction de polluants organiques de l'eau peut s'avérer efficace, comme c'est le cas des MOFs à base de zirconium UiO-66 qui ont révélé un effet adsorbant important sur les BTEX [2].

Les sources de MOF sont multiples. Ainsi pour des raisons environnementales, les matériaux utilisés dans cette étude proviennent du recyclage de batteries Li-ion. Cependant, la synthèse de MOF conduit généralement à l'obtention d'un matériau sous forme de poudre, ce qui s'avère peu adapté à l'application industrielle. Les recherches actuelles s'accentuent donc sur la mise en forme des MOFs sur supports solides et ainsi que sur leur assemblage sous forme monolithique.

L'une des voies possible consiste réaliser un monolithe à partir d'émulsions de Pickering. Les émulsions de Pickering sont des émulsions stabilisées par des particules solides, des MOFs dans cette étude, qui s'adsorbant à l'interface phase aqueuse – phase organique. Dans le cas d'émulsions à haute phase interne (HIPE), ces dernières apparaissent sous l'aspect d'un gel et peuvent alors être utilisées en tant que « template » pour la synthèse de matériaux monolithiques macroporeux. La phase organique peut être éliminée grâce à des traitements spécifiques (CO_2 supercritique par exemple) et la taille des gouttelettes définit alors la porosité finale du monolithe. [3]

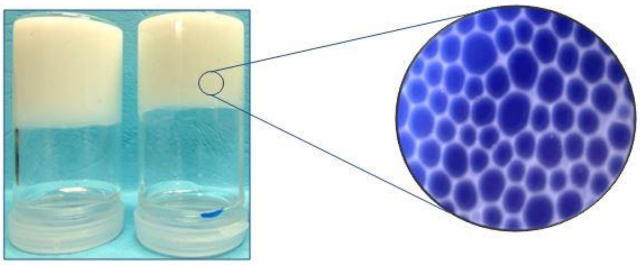


Figure 2: Gel résultant d'une émulsion de Pickering-HIPE avant séchage au CO_2 supercritique

[1] H.Furukawa , *Science* **2013,** vol. 341.

[2] Amador. RN., Cirre L., Carboni M. et Meyer D., *Journal of Environmental Management* **2018**, vol. 214, pp. 17-22.

[3] Zhang B. *et al*, *Scientific Reports* **2016**, vol. 6.

Catalytic reductive depolymerization of wood lignin and waste plastics into chemicals

Louis Monsigny, Elias Feghali, Jean-Claude Berthet, Thibault Cantat

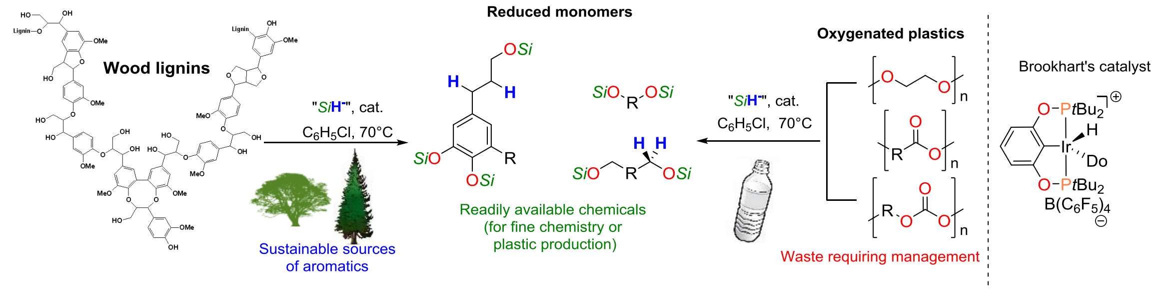
CEA Saclay, IRAMIS, UMR CEA-CNRS UMR 3685, Université Paris-Saclay, 91191, Gif-sur-Yvette, France.
Email: *jean-claude.berthet@cea.fr; louis.monsigny@cea.fr; thibault.cantat@cea.fr*

Most of the organic chemicals and 99,9% of the aromatics compounds are derived from petrochemistry. The deleterious environmental impact of human activities and depletion of raw material fossils impose the design of sustainable processes to decorelate the chemical industry from its fossil fuel dependance. It is thus crucial to find alternatives resources, natural and renewable, to access major intermediates for industrial applications and high added values chemicals. The future of chemical industry turns on the valorization of biomass together with the recyclability of matters. [1,2]

Wood lignin is an amorphous, polymeric and strongly ether-linked material, extracted in tons by paper industry and currently burnt for energy production. Because of its high content in aromatic compounds, this natural material has a huge potential for the production of aromatic chemicals in particular low molecular weight molecules (benzene, toluene, xylenes) which market is estimated to be close to 100 billions in 2015. This is however a challenging task that requires a change of paradigm and the design of novel processes for the selective depolymerization of lignin into a limited number of molecules. In 2014, our laboratory reported a successful route for depolymerisation of lignin based on a convergent reducing route with silanes (reductants) and tris(pentafluorophenyl)borane $B(C_6F_5)_3$ as catalyst. By this way, a few number of pure aromatic compounds have been isolated for the first time from a variety of softwood (resinous trees) and hardwood (leaved trees) lignins.[3]

The ability to cleave strong C–O bonds by this approach was viewed as promising for the destructuration of other common oxygenated polymers and in particular for the management of a variety of manufactured oxygenated polymers. This route was succesfully applied to the depolymerization of oxygenated plastics containing ethereal, ester and carbonates moieties.

Because of the poor stability of the organic compound $B(C_6F_5)_3$ in common organic solvents, we searched its replacement with a more stable metal complex. Our choice focused on the Brookhart's iridium(III) complex which chemical behaviour in hydrosilylation is close to that of $B(C_6F_5)_3$ and we drawn comparizons between these two catalysts.[4]



Catalytic hydrosilylation of wood lignins (left) and oxygenated plastics (right) with iridium(III) complex

Acknowledgements: We acknowledge CEA, CNRS and ERC (Starting Grant Agreement n.336467)

[1]. F. G. Calvo-Flores et al, in *Lignin and lignans as renewable raw materials: Chemistry, Technology and Applications*, ed. C.V Steven, Wiley-Blackwell, **2015**.

[2]. a) PlasticsEurope: Plastics The Facts **2017**; b) World Economic Forum, Ellen MacArthur Foundation, The New Plastics Economy – Catalysing Action, **2017.**

[3]. E. Feghali, T. Cantat T., *Chem. Commun.*, **2014**, *50*, 862. b) E. Feghali, G. Carrot, P. Thuéry, C. Genre, T. Cantat, *Energy Environ. Sci.*, **2015**, *8*, 2734. c) E. Feghali, T. Cantat, *ChemSusChem*, **2015**, *8*, 980.

[4]. a) L. Monsigny, E. Feghali, J.-C Berthet, T. Cantat, *Green Chem.*, **2018**, *20*, 1981 (Lignin).; b) L. Monsigny, J.-C. Berthet, T. Cantat, *ACS Sustainable Chem. Eng.*, **2018**, *6*, 10481 (plastics).

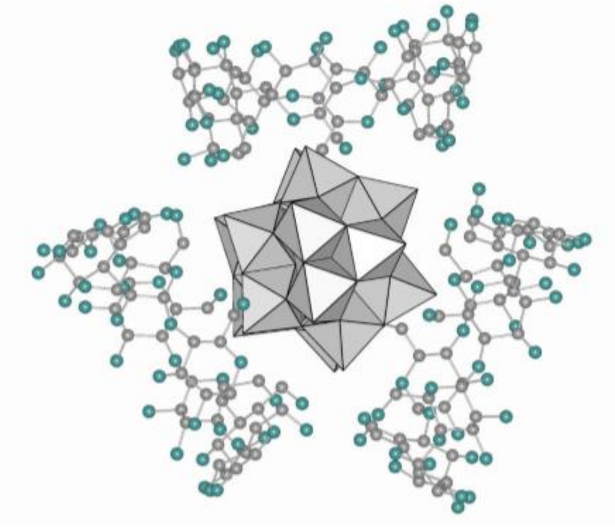
Supramolecular assemblies between Polyoxometalates and γ-Cyclodextrin

Nathalie Leclerc-Laronze, Anton A. Ivanov, Clément Falaise, Mohamed Haouas,
Jérôme Marrot, Emmanuel Cadot

Institut Lavoisier de Versailles, CNRS UMR 8180, UVSQ, Université Paris-Saclay,
45 avenue des Etats-Unis 78035 Versailles, France
nathalie.leclerc@uvsq.fr

The reactivity between archetypal polyoxometalates (POMs) (Dawson $[P_2W_{18}O_{62}]^{6-}$, Keggin $[XW_{12}O_{40}]^{n-}$ or Preyssler $[P_5W_{30}O_{110}]^{15-}$ type anions, X = B, Si or P) and γ-cyclodextrin (γ-CD) will be presented in this communication. POMs and γ-CD exhibit specific interactions leading to the formation of supramolecular assemblies as observed by single-crystal X-ray diffraction analysis. Structural analysis reveals the CDs can interact with primary or secondary face depending on the nature of the POM.

Interestingly, solution investigation conducted by a set of complementary methods such as multinuclear NMR (^{1}H, ^{31}P), ESI Mass and ITC measurements, reveals the host-guest pre-associations exist also in solution. The supramolecular complexation of POMs involves modification of intrinsic properties as observed by electrochemical analysis (cyclic voltammetry).



Structural representation of the supramolecular POM@3γ-CD.

[1]. M.A. Moussawi, N. Leclerc-Laronze, S. Floquet, P. A. Abramov, M. N. Sokolov, S. Cordier, A. Ponchel, E. Monflier, H. Bricout, D. Landy, M. Haouas, J. Marrot, E. Cadot, *J. Am. Chem. Soc.* **2017**, *139*, 12793–12803.

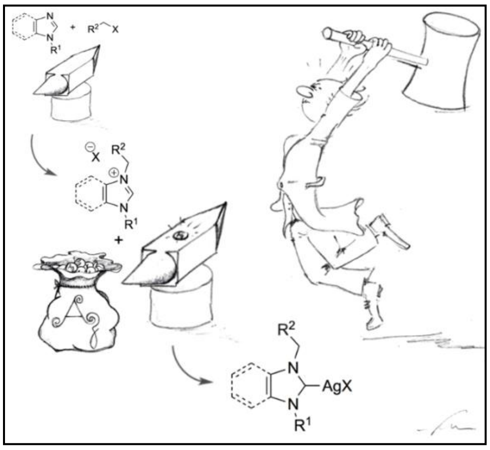
Unraveling the synthesis of NHC-metal complexes using mechanochemistry

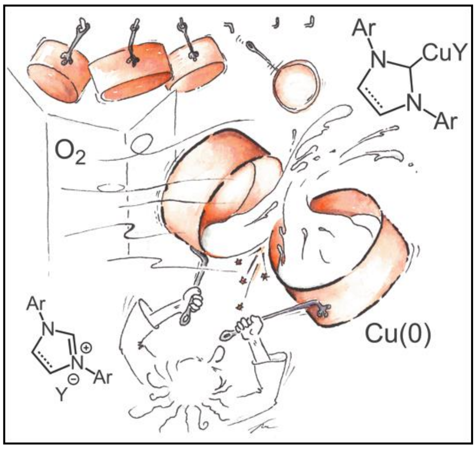
François Quintin[a], Audrey Beillard[a], Xavier Bantreil[a], Thomas-Xavier Métro[a], Jean Martinez[a] and Frédéric Lamaty[a]

[a]*Green Chemistry and Enabling Technologies (www.greenchem.um2.fr)*
Département des Acides Aminés, Peptides et Protéines
Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, CNRS, Université de Montpellier,
ENSCM, Campus Triolet, Place Eugène Bataillon,
34095 Montpellier cedex 5, France

e-mail: francois.quintin@umontpellier @frquintin

Due to their stability associated to their excellent catalytic properties, NHC-metal complexes (NHC= N-Heterocyclic Carbene) have been extensively used for a wide range of reactions. However, their syntheses in solution are highly substrate-dependent and require long reaction times and excess of reagents. A convenient way to increase the efficiency and to reduce the environmental impact of these reactions in order to develop a more general and user-friendly procedure is to use solvent-free mechanosynthesis.[1] The absence of solvent associated with intensive mechanical agitation allowed to access a wide range of valuable NHC-metal complexes and apply them in catalysis.[2]





[1] (a) N. R. Rightmire T. P. Hanusa, Dalton Trans. **2016**, *45*, 2352-2362; (b) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413-447.

[2] (a) A. Beillard, E. Golliard, V. Gillet, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *Chem. Eur. J.* **2015**, *21*, 17614-17617; (b) A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *New J. Chem.* **2017**, *41*, 1057-1063; (c) A. Beillard, T.-X. Métro, X. Bantreil, J. Martinez, F. Lamaty, *Chem. Sci.* **2017**, *8*, 1086-1089; (d) A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *Dalton Trans.* **2016**, *45*, 17859-17866; (e) A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *Green Chem.* **2018**, *20*, 964-968; [f] A. Beillard, T.-X. Métro, X. Bantreil, J. Martinez, F. Lamaty, *Eur. J. Org. Chem.* **2017**, 4642-4647.

Air-promoted and Ligand-free Manganese-Catalyzed Homocoupling of Aryllithium Compounds

Yassir Zaid,†,§ Yujia Liu,† Julien Bergès,† Fouad Ouazzani Chahdi,§ Arie Van Der Lee,‡ Dominique Harakat,∇ Eric Clot,† Florian Jaroschik,† and Marc Taillefer*,†

† Institut Charles Gerhardt Montpellier, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

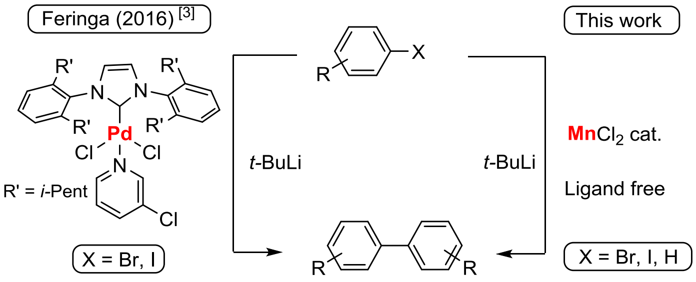
∇ Institut de Chimie Moléculaire de Reims, Université de Reims, BP 1039, 51687 Reims, France

§ Laboratoire chimie organique appliquée LCOA, Faculté des Sciences et Techniques, 30000 Fès, Maroc

‡ Institut Européen des Membranes, ENSCM, Université de Montpellier, 34095 Montpellier, France.

e-mail : yassir.zaid@enscm.fr

Biaryl units are widely found in numerous natural products, biologically active compounds, agrochemicals, commercial dyes, organic conductors and semi-conductors.[1] To construct this family of compounds, transition-metal-catalyzed coupling reactions, employing various organometallic compounds such as organostannanes (Stille coupling), organoboranes (Suzuki coupling), organozincs (Negishi coupling), organomagnesiums (Grignard regent) or organosilanes (Hiyama coupling), are among the most powerful tools.[2] Since the last decade, organolithiums attract much attention because of their high reactivity, commercial availability and are also used for biaryl synthesis via transition-metal catalyzed coupling raction. Recently, Feringa et al. have described a sophisticated palladium-catalyzed system to perform homocoupling reaction from aryl halides using organolithium (Scheme 1).[3] Here, we present a very simple manganese-catalyzed system to realize this type of reaction involving organolithium reagents starting from aryl halides (halide/lithium exchange) and arenes (direct C-H activation). Compared with palladium, manganese is cheaper, much more abundant and less toxic transition metal, hence an excellent alternative to precious metals for homogenous catalysis.[4] Our catalytic system was successfully applied with various substrates to give the corresponding symmetrical biaryls in excellent yields. Moreover, ESI-MS and DFT have been performed and interpret the reaction mechanism.



Scheme.1 Transition-metal-catalyzed homocoupling of aryl halides in the presence of alkyllithium.

[1]. a) Cepanec, I. (Ed.) in synthesis of biaryls; Elsevier Ltd.; Oxford, **2004**; b) Boldi, A. M.; Curr. Opin. Chem. Biol. **2004**, 8, 281-286; c) M. B. Nielsen, F. Diederich, Chem. Rev. **2005**, 105, 1837-1868; d) M. Kertesz, C. H. Choi, S. Yang, Chem. Rev. **2005**, 105, 3448-3481.
[2]. Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. Chem. Rev. **2002**, 102, 1359-1470.
[3]. Buter, J.; Heijnen, D.; Vila, C.; Hornillos, V.; Otten, E.; Giannerini, M.; Minnaard, A. J.; Feringa, B. L. Angew. Chem. Int. Ed. **2016**, 55, 3620-3624.
[4]. Carney, J. R.; Dillon, B. R.; Thomas, S. P. Eur. J. Org. Chem. **2016**, 3912-3929.

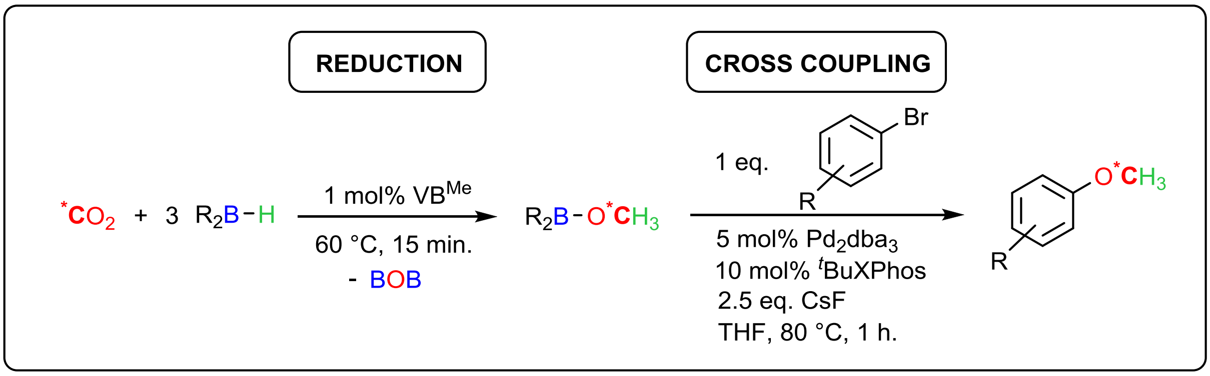
New Catalytic Reactions using CO_2 for Radiolabeling of Tracers

Alexia Ohleier,[a] Davide Audisio,[b] Fabien Caillé[c], Thibault Cantat.[a]

[a] CEA Saclay - IRAMIS/NIMBE/LCMCE, 91191 Gif sur Yvette Cedex. [b] CEA Saclay - DRF/JOLIOT/SCBM/LMC, 91191 Gif sur Yvette Cedex. [c] CEA - SHFJ, 4 Place du Général Leclerc, 91401 Orsay Cedex
e-mail : alexia.ohleier@cea.fr

CO_2, well known as a greenhouse gas responsible for global warming and considered as a cheap, non-toxic, renewable C1 building block, is the only primary carbon source for all carbon labeled compounds. Though its kinetic and thermodynamic stability significantly restrains potential applications. Broader availability of secondary labeled carbon sources would therefore grant access to a wide array of highly functionalized bioactive tracers. Indeed, ^{14}C labelled compounds are commonly required during the development process of drugs where as ^{11}C tracers are used for PET scan imaging.

In this context, we have been investigating CO_2 reduction into methoxy derivatives followed by a Suzuki cross-coupling to generate anisoles moieties. Selective borane mediated organocatalytic CO_2 reduction into OMe synthons has been previously disclosed by our group.[1] However, very few couplings between methanol derivatives and aryl halides have been reported to date.[2] Inspired by Novak's work,[3] an innovative, efficient palladium catalyzed cross-coupling between methoxyboranes and aryl bromides has been developed under mild conditions. Working in a double chamber set-up allows both reactions to be compatible. This strategy is further expected to be tested on therapeutic targets and ideally transposed to ^{14}C and ^{11}C isotopes.



[1]. E. Blondiaux, J. Pouessel, T. Cantat, *Angew. Chem. Int. Ed.*, **2014**, *53*, 12186 - 12190.
[2]. (a) K. E. Torraca, X. Huang, C. A. Parrish, S. L. Buchwald, *J. Am. Chem. Soc.*, **2001**, *123*, 10770 - 10771. (b) E. J. Milton, J. A. Fuentes, M. L. Clarke, *Org. Biomol. Chem.*, **2009**, *7*, 2645 - 2648. (c) S. Gowrisankar, H. Neumann, M. Beller, *Chem. Eur. J.,* **2012**, *18*, 2498 - 2502.
[3]. G. L. Tolnai, B. Pethő, P. Králl, Z. Novák, *Adv. Synth. Catal.*, **2014**, *356*, 125 - 129.

Making Prussian blue analogues nanoparticles luminescent: effect of the confinement over the properties.

E. Mamontova,[a] J. Long,[a] R. A.S. Ferreira,[b] A. M. P. Botas,[b]
F. Salles,[c] Y. Guari,[a] L. D. Carlos[b] and J. Larionova[a]

[a]Institut Charles Gerhardt, Equipe Ingénierie Moléculaire et Nano-Objets, UMR 5253 Université de Montpellier, ENSCM, CNRS. Place Eugène Bataillon, 34095 Montpellier Cedex 5, France;
[b]Department of Physics and CICECO Aveiro - Institute of Materials, University of Aveiro, 3810-193, Aveiro, Portugal.
[c]Institut Charles Gerhardt Montpellier, UMR 5253, Agrégats, Interfaces et Matériaux pour l'Energie ENSCM/CNRS/UM, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France.
e-mail : ekaterina.mamontova@umontpellier.fr

Multifunctional molecular materials combining several useful physical or chemical properties have attracted a great deal of attention in the recent years due to their fundamental interest and potential applications. Recent advances have been made by combining magnetism with optical activity, porosity, electron switching or ferroelectricity. Surprisingly, less effort has been devoted to the synthesis of molecular magnets exhibiting photoluminescence due to the quenching of this properties by paramagnetic transition metal ions.

To address this problem, an increasing interest can be observed for the design of nanostructures involving coordination polymers known also as Metal Organic Frameworks (MOFs) or Prussian Blue Analogous (PBAs). In this sense, we present here a new synthetic strategy to design multifunctional magneto-optical nanomaterials combining PBA nanostructures and luminescent ligands. Molecular simulations confirm the adsorption mechanisms of luminophore while the magnetic and photoluminescence properties were investigated in details and reveal that both functionalities are preserved upon ligand adsorption. The proposed methodology could be extended to various functional guests and different PBA in order to design multifunctional nanoprobes.

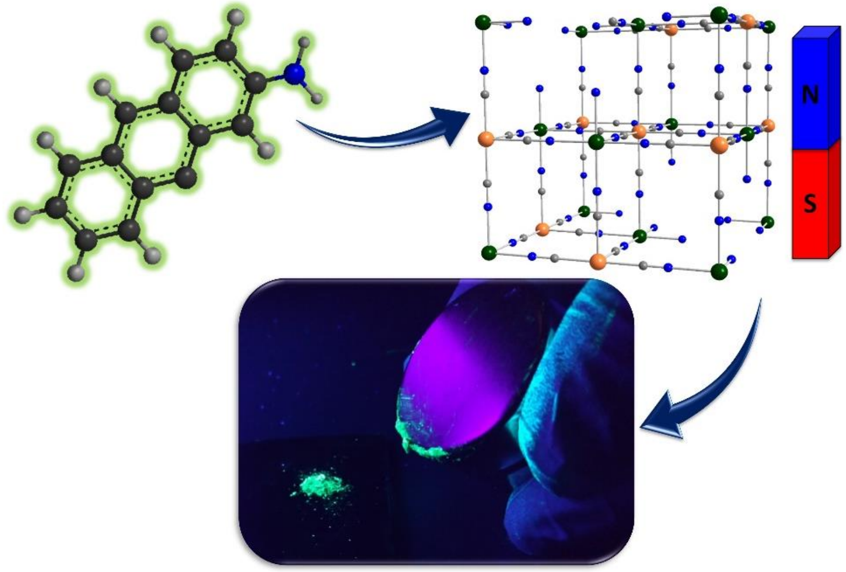


Figure 1. Schematic representation of the synthetic strategy used in the post-synthetic functionalization of PBA nanoparticles with final photograph of functionalized nanoparticles interacting with a magnet at room temperature under excitation with UV lamp at 365 nm.

Photophysical properties of 5-substituted-1,10-phenanthroline ligands and related Ru(II) edifices

Sylviane Chevreux,[a] Elodie Rousset,[a] Gilles Lemercier.[a]

Université de Reims Champagne Ardenne,
ICMR UMR CNRS 7312 BP 1039 – 51687 Reims cedex 2, France
e-mail : gilles.lemercier@univ-reims.fr

Our research concerns fundamental aspects and potential applications of molecular and (self-organized)[1] supramolecular edifices. We will described: (*i*) the huge solvatochromism of 5-substituted-1,10-phenanthroline derivatives and related materials[2] which give them interesting properties for applications as optical sensors; one compound exhibits a solvent-tuned dual emission in protic[3] and aprotic solvent[4] (*ii*) related fluorenyl Ru(II) complexes-based ^{3}MLCT excited-states and their absorption and lifetime properties for several applications such as two-photon excited luminescence or photodynamic therapy (2PE-PDT),[5] and optical power limiting[6] (*iii*) multifunctional nano-edifices[7] with novel properties; a switch from 2P absorption of Ru(II) coordination complexes to saturable absorption for the related decorated-gold nanoparticles has been highlighted.[8]

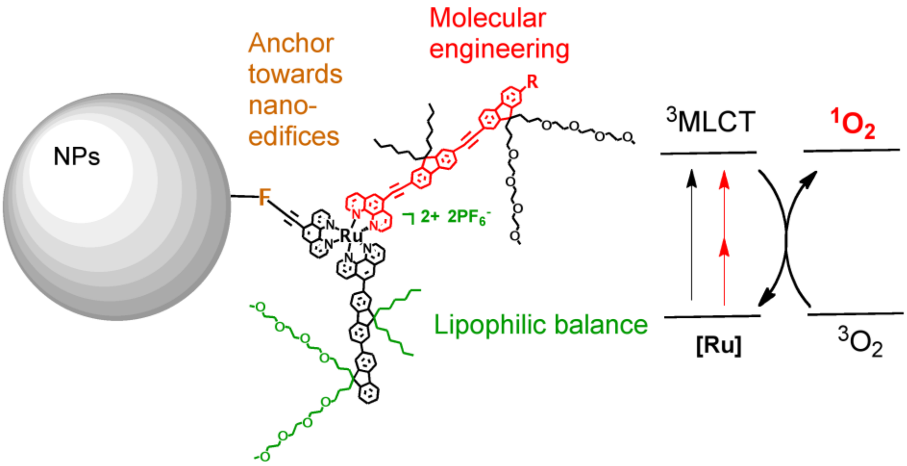


Figure 1: [Ru(II)] complexes as versatile (nano-)platfoms for applications

[1] Van Q. Nguyen, X. Sun, F. Lafolet, J.-F. Audibert, F. Miomandre, G. Lemercier, F. Loiseau, J.-C. Lacroix, *J. Am. Chem. Soc.*, **2016**, *138*, 9381.
[2] J. Guérin, C. Aronica, G. Boeuf, J. Chauvin, J. Moreau, G. Lemercier, *J. Lumin.*, **2011**, *131*, 2668.
[3] S. Chevreux, C. Allain, L. Wilbraham, K. Nakatani, P. Jacques, I. Ciofini, G. Lemercier, *Faraday Disc.*, **2015**, *185*, 285.
[4] S. Chevreux, R. Paulino Neto, C. Allain, K. Nakatani, P. Jacques, I. Ciofini, G. Lemercier, *PhysChemChemPhys.* **2015**, *17*, 7639.
[5] C. Boca, M. Four, A. Bonne, B. van Der Sanden, S. Astilean P. L. Baldeck, G. Lemercier *Chem. Commun.*, **2009**, 4590.
[6] M. Four, D. Riehl, O. Mongin, M. Blanchard-Desce, L. M. Lawson-Daku, J. Moreau, J. Chauvin, J. A. Delaire, G. Lemercier, *PhysChemChemPhys.*, **2011**, *13*, 17304.
[7] C. Truillet, F. Lux, J. Moreau, M. Four, L. Sancey, S. Chevreux, G. Boeuf, P. Perriat, C. Frochot, R. Antoine, P. Dugourd, C. Portefaix, C. Hoeffel, M. Barberi-Heyob, C. Terryn, L. van Gulick, G. Lemercier, O. Tillement *Dalton Trans.*, **2013**, *42*, 12410.
[8] J. Moreau, F. Lux, M. Four, J. Olesiak-Banska, K. Matczyszyn, P. Perriat, C. Frochot, P. Arnoux, O. Tillement, M . Samoc, G. Ponterini, S. Roux, G. Lemercier, *PhysChemChemPhys.*, **2014**, *16*, 14826.

Synthèse et Caractérisation de Porphyrines Conjuguées à des Complexes d'Or(I) avec des Ligands Carbènes N-Hétérocycliques

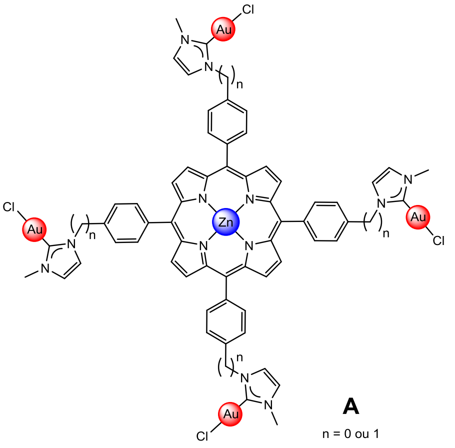
Clémence Rose, Sébastien Clément, Sébastien Richeter

Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM, CC 1701,
Place Eugène Bataillon, 34095 Montpellier
e-mail : clemence.rose@etu.umontpellier.fr, sebastien.richeter@umontpellier.fr

Les porphyrines sont des macrocycles tétrapyrroliques aromatiques pouvant complexer divers cations métalliques au sein de leur cavité centrale. Les complexes obtenus sont communément nommés *métalloporphyrines*. Ces métaux *internes* peuvent être utilisés comme sites catalytiques mais aussi en tant que sites de coordination pour la construction d'assemblages multiporphyriniques. Ces assemblages peuvent être très variés allant de simples dimères de porphyrines jusqu'à des polymères de coordination.

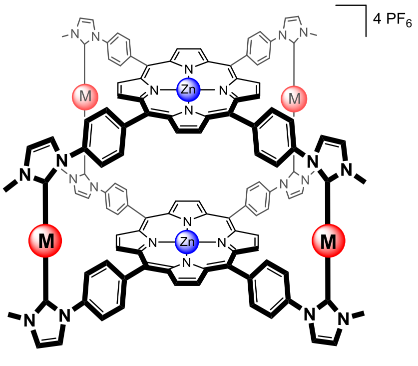
Les avancées continues sur la fonctionnalisation des positions *β*-pyrroliques et *méso* ont également permis l'obtention des dérivés de porphyrines comportant des sites de coordination *externes* en plus du site de coordination *interne*. Ces composés offrent de nouvelles possibilités dans la fonctionnalisation des porphyrines par des complexes métalliques, en vue d'applications dans les domaines de la catalyse,[1] de l'électronique moléculaire[2] et de la biomédecine.[3]

A travers ce poster, seront exposés nos travaux récents sur des porphyrines fonctionnalisées en positions *méso* par des ligands carbènes N-hétérocycliques permettant d'y lier jusqu'à quatre complexes métalliques en plus du métal interne (complexes pentamétalliques : 1 métal *interne* + 4 métaux *externes*). Nous décrirons la synthèse de complexes d'or(I) **A**, ainsi que la synthèse de dimères de porphyrines cofaciales **B** assemblées par quatre cations métalliques[4] comme représentés ci-dessous. Ces dimères de porphyrines cofaciales de type *cage* ouvrent des perspectives intéressantes, notamment dans le but d'encapsuler de petites molécules π-conjuguées planes.



A

n = 0 ou 1



B

M = Au or Ag

[1]. G. H. Ananthnag, V. S. Shetti, *Chem. Soc. Rev*., **2017**, *46*, 14062.
[2]. M. Abdelhameed, A. Langlois, P.-L. Karsenti, S. Richeter, R. Ruppert, P. D. Harvey, *Chem. Commun*., **2014**, *50*, 14609.
[3]. J.-F. Longevial, K. El Cheikh, D. Aggad, A. Lebrun, A. van der Lee, F. Tielens, S. Clément, A. Morère, M. Garcia, M. Gary-Bobo, S. Richeter, *Chem. Eur. J.*, **2017**, *23*, 14017.
[4]. C. Rose, A. Lebrun, S. Clément, S. Richeter, *Chem. Commun*., **2018**, *54*, 9603.

Copper Mediated Acetoxylation of Diaryliodonium Salt

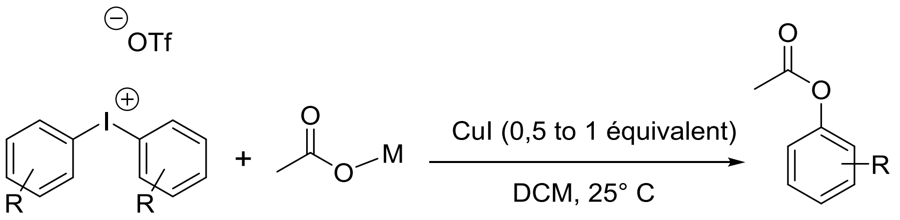
Mohamed Rami Chebbi [a, c], Anis Tlili [b], Mohamed Lotfi Efrit [a], Marc Taillefer [c*]

a) Université Tunis El Manar, Faculté des sciences de Tunis, Département de chimie, laboratoire de Synthèse Organique Sélective et Hétérocyclique et Evaluation d'Activité Biologique LR17ES01, Campus universitaire 2092 El Manar Tunisie
b) Université Claude Bernard - Lyon 1, 43 Bd du 11 novembre 1918, Bat. Raulin (4ème étage), 69622 Villeurbanne Cedex – France
c) Ecole Nationale Supérieure de Chimie de Montpellier, Institut Charles Gerhardt, CNRS, UMR 5253, AM2N 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France
E-mail : mohamed-rami.chebbi@enscm.fr

The acetoxy group acts as a functional group modifier while imparting polar nature to a molecule. It is ubiquitous in a plethora of prodrugs, natural products, antimicrobial agents, and herbicidal materials. [1]

Newer methods of regiospecifically introducing this group in organic molecules continues therefore to be of relevance.

In this work we present a new method of copper mediated aryl acetoxylation under mild conditions with the diaryliodonium salts as aryl source for the first time.



R= EWG, DG
M= Metal

[1]: a) R. Rais, J. Vávra, T. Tichý, R. P. Dash, A. J. Gadiano, L. Tenora, L. Monincova, C. Barinka, J. Alt, S. C. Zimmermann, C. E. Slusher, Y. Wu, K. Wozniak, P. Majer, T. Tsukamoto, B. S. Slusher, J. Med. Chem. 2017, 60, 7799. b) L. D. Patterson, M. J. Miller, J. Org. Chem. 2010, 75, 1289.

ROS production by copper complexes with N-truncated Aβ peptides

Charlène Esmieu,[a] Guillaume Ferrand,[a] Valentina Borghesani,[a] Christelle Hureau[a]

[a]Laboratoire de Chimie de Coordination (LCC), 205 Route de Narbonne, 31400 Toulouse, France
e-mail : charlene.esmieu@lcc-toulouse.fr

Alzheimer's disease (AD) is a neurodegenerative disease and the major cause of dementia throughout the world that makes it one of the biggest challenges of the 21st century in public health. The prevalence of this disease is expected to increase rapidly in the coming decades. Although the mechanisms underlying this complex pathology are not yet fully understood, a broad consensus attributes the early development of AD to a so called amyloid cascade. This deleterious process relies on the disturbed equilibrium between the production of a peptide called amyloid-β (Aβ) and its degradation by other proteases. This results in a significant increase in extracellular concentration, leading to its aggregation *via* the formation of oligomers, protofibrils and fibrils. [1] These assemblages come together to form amyloid plaques, a distinctive post-mortem marker of the disease. Different forms of Aβ peptides are found in the senile plaques, such as the "full-length" $A\beta_{1-40/42}$ peptide and the N-truncated peptides $A\beta_{n-40/42}$ (position 1 to 5).[2,3] Strong evidences have associated the high toxicity of Cu-containing aggregates to their ability to promote the oxidative stress observed in AD *via* the catalytic production of reactive oxygen species (ROS). [4,5] A lot have been done regarding the studies of the ROS production with the full length Aβ peptide, [6] nevertheless N-truncated forms which are little considered are of interest because it's thought that there are present in huge quantity in the brain and senile plaques. [3,7] Moreover it's admitted that they possess a protective effect against ROS production thank to their ATCUN type coordination site. Indeed, the coordination site of the N-truncated peptides is different from the one in $A\beta_{1-40/42}$ (Figure1) which confers them different properties regarding the ROS production. [8] Here we present the results of the study of the ROS production obtained with two N-term Aβ isoforms found in the brain: $A\beta_{4-n}$ and $A\beta_{11-n}$. This study aims to clarify/investigate the following points: (i) the ROS production of $Cu^{II/I}A\beta_{4/11-16}$ in our experimental conditions, and (ii) the effect of the presence of $A\beta_{4/11-n}$ on the ROS production by $Cu^{II/I}A\beta_{1-16}$.

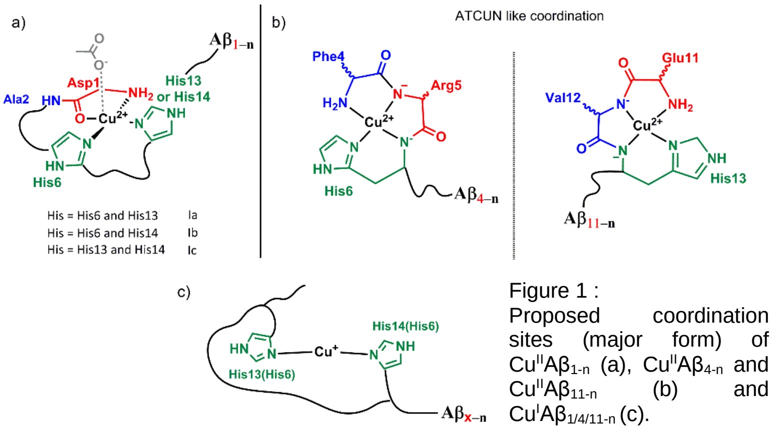


Figure 1 : Proposed coordination sites (major form) of $Cu^{II}A\beta_{1-n}$ (a), $Cu^{II}A\beta_{4-n}$ and $Cu^{II}A\beta_{11-n}$ (b) and $Cu^{I}A\beta_{1/4/11-n}$ (c).

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[1].Kozlowski, H.; Luczkowski, M.; Remelli, M.; Valensin, D. *Coordination Chemistry Reviews* **2012,** *256* (19-20), 2129-2141.
[2].Bayer, T. A.; Wirths, O., *Acta Neuropathologica* **2014,** *12è*, 787-801.
[3].Lewis, H.; Beher, D.; Cookson, N.; Oakley, N.; Piggott, M.; Morris, C. M.; Jaros, E.; Perry, R.; Ince, P.; Kenny, R. A.; Ballard, C. G.; Shearman, M. S.; Kalaria, R. N., *Neuropathology and Applied Neurobiology* **2006,** *32*, 103-118.
[4].Kenche, V. B.; Barnham, K. J., *British Journal of Pharmacology* **2011,** *163* (2), 211-219.
[5].Cheignon, C.; Tomas, M.; Bonnefont-Rousselot, D.; Faller, P.; Hureau, C.; Collin, F., *Redox Biology* **2018,** *14*, 450-464.
[6].Hureau, C., *Coordination Chemistry Reviews* **2012,** *256* (19-20), 2164-2174.
[7].Liu, K.; Solano, I.; Mann, D.; Lemere, C.; Mercken, M.; Trojanowski, J. Q.; Lee, V. M., *Acta Neuropathol.* **2006,** *112* (2), 163-174.
[8].Borghesani, V.; Alies, B.; Hureau, C., *European Journal of Inorganic Chemistry* **2018**, 7-15.

Aminophosphonates derivatives as potential biological agents

Aneta Kosińska,[†] David Virieux,[§] Jean-Luc Pirat,[§] Kamila Czarnecka,[‡] Małgorzata Girek,[‡] Paweł Szymański,[‡] and Bogna Rudolf[†]

[†] Department of Organic Chemistry, University of Lodz, Tamka 12, 91-403 Łódź, Poland

§ Institut Charles Gerhardt Montpellier, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

[‡] Department of Pharmaceutical Chemistry, Drug Analyses and Radiopharmacy, Faculty of Pharmacy, Medical University of Lodz, Muszynskiego 1, 90-151 Łódź, Poland

e-mail : kosinskaneta@wp.pl

Aminophosphonates derivatives are consider as biological agents because of their structural similarity to amino acids and presence of the phosphorus atom in their structure.[1-2]

We have reported previously that the half-sandwich iron phosphonate complexes derived from $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}N\text{-maleimidato})$ are able to inhibit serine hydrolases by phosphorylation of the active site serine residue.[3] Cholinesterase inhibitors (ChEIs) were the first and are the only class of drugs in the market that showed some results in the treatment of Alzheimer's disease.

Herein, we present the design and synthesis of aminophosphonates and new metallocarbonyl aminophosphonate derivatives. Obtained aminophosphonates were then tested on cholinesterases and neuroblastoma cells. The determination of the acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) inhibitory capacity of the newly synthesized compounds was performed by an adaptation of the spectroscopic method described by Ellman.[4] To the neuroblastoma cells analysis we used the MTT test. Results allowed to verify, if compounds are safe for neuronal cell line and be useful to treat neurodegenerative diseases.

[1]. A.K. Bhattacharya, D.S. Raut, et all., *Eur. J. Med. Chem.*, **2013**, *66*, 146-152.
[2]. P. Kafarski, J. Zoń, *Aminophosphonic and Aminophosphinic Acids*, **2000**, 33-102.
[3]. B. Rudolf, J. Zakrzewski, M. Salmain, G. Jaouen, *New. J. Chem.*, **1998**, *22*, 813-818.
[4]. Rangappa S. Keri, et all., *Bioorganic & Medicinal Chemistry*, **2013**, *21*, 4559–4569.

Electronic and photovoltaic properties of conjugated compounds based on pyridine candidates for organic solar cell applications.

T. Abram, R. Kacimi, L. Bejjit, M. Bouachrine

MEM, High School of Technology (ESTM), University Moulay Ismail, Meknes, Morocco.
E-mail: tayeb87abram@gmail.com or bouachrine@gmail.com;

The search for renewable energy currently leads the development of photovoltaic cells where organic conductive materials can play a vital role due to their ability to separate the electron-hole pairs and carry these loads to the electrodes in specific electronic configurations.
In this work, a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on pyridine. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO and energy Egap of the studied compounds have been calculated and reported. These properties suggest these materials as good candidates for organic solar cells.

Keywords:

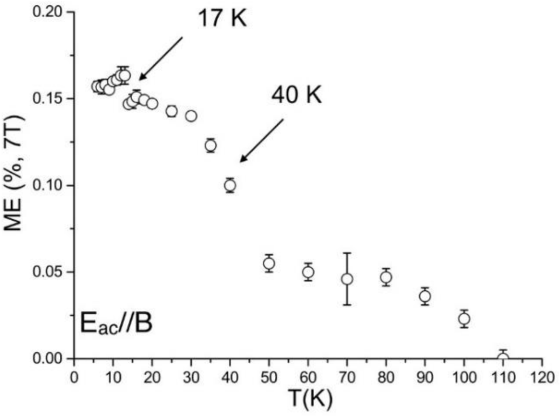
Pyridine, organic solar cells, electronic properties, HOMO, LUMO, Egap.

Fonctionnalisation d'hydroxydes simples lamellaires par des fluorènes-phosphonates : synthèse, caractérisations et étude des propriétés diélectriques

Quentin Evrard[a], Ziyad Chaker[b], Mélissa Roger[c], Charlotte M. Sevrain[c], Emilie Delahaye[b], Cédric Leuvrey[b], Guido Ori[a], Jean-Michel Rueff[d], Pierre Rabu[b], Alain Pautrat[d], Tathamay Basu[d], Paul-Alain Jaffrès[c], Guillaume Rogez[b]

[a] ISCR-INSA-Rennes, 20 av.des buttes de Coësmes, CS 70839 35708 RENNES Cedex 7, France
[b]Institut de Physique et Chimie de Strasbourg, Université de Strasbourg and CNRS, UMR 7504, 23 rue du Loess, BP43, 67034 Strasbourg cedex, France
[c] Laboratoire de Chimie Électrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521, 6 av. V. Le Gorgeu, 29238 Brest cedex 03, France
[d] Laboratoire CRISMAT, Bd du Maréchal Juin, 14050 Caen cedex, France
e-mail : quentin.evrard@insa-rennes.fr

Depuis la découverte des propriétés exceptionnelles des dérivés de graphène, la recherche dans le domaine des nanomatériaux fonctionnels a apporté une attention croissante à la conception de nouveaux systèmes multifonctionnels basés sur des nano-feuillets. Parmi les possibles voies de synthèse, l'approche des hybrides organiques-inorganiques c'est avérée être idéale pour apporter la multifonctionnalité au sein d'un seul et unique matériau. De cette façon, les hydroxydes simples lamellaires de métaux de transition (HSL) de formule générale $M^{II}_2(OH)_3(X)\cdot mH_2O$ (M = Co,Cu,Ni et X = nitrate, acétate…), sont des matériaux de choix pour les réactions de greffage de multiples molécules.[1] Cette communication par poster présente le travail de fonctionnalisation de ces composés par des molécules portant des fonctions d'accroche acide phosphoniques, ce qui n'a été que rarement décrit. Nous démontrerons aussi la pertinence de la stratégie de préintercalation[2] pour insérer ce type de molécules et pour obtenir les hybrides désirés avec une bonne cristallinité. Leurs propriétés magnétiques ainsi que de couplage magnétodielectrique seront également présentées (voir figure).[3]



Magnétocapacitance relative obtenue à 7 T d'un HSL fonctionnalisé en fonction de la température.

[1]. Shimizu, H.; Okubo, M.; Nakamoto, A.; Enomoto, M.; Kojima, N. *Inorg. Chem.* **2006**, *45*, 10240-10247; [b]Bourzami, R.; Eyele-Mezui, S.; Delahaye, E.; Drillon, M.; Rabu, P.; Parizel, N.; Choua, S.; Turek, P.; Rogez, G. *Inorg. Chem.* **2014**, *53*, 1184-1194.
[2]. Delahaye, E.; Eyele-Mezui, S.; Bardeau, J.-F.; Leuvrey, C.; Mager, L.; Rabu, P.; Rogez, G. *J. Mater. Chem.* **2009**, *19*, 6106-6115.
[3]. Q. Evrard, Z. Chaker, M. Roger, C. M. Sevrain, E. Delahaye, M. Gallart, P. Gilliot, C. Leuvrey, J.-M. Rueff, P. Rabu, C. Massobrio, M. Boero, A. Pautrat, P.-A. Jaffrès, G. Ori and G. Rogez, *Adv. Func. Mater.*, **2017**, *27*, 1703576-1703589.

Lanthanoid Complexes with Crown Ether and Catecholate Ligands: Interplay of Raman and Anomalous Phonon Bottleneck Processes

Elodie Rousset,[a] Matteo Piccardo,[b] Marie-Emmanuelle Boulon,[b] Robert W. Gable,[a] Lorenzo Sorace,[b] Alessandro Soncini,[a] Colette Boskovic.[a]

[a] *School of Chemistry, University of Melbourne, Australia*
b UdR INSTM and Department of Chemistry "U. Schiff", University of Florence, Italy

e-mail : elodie.rousset@univ-reims.fr

The combination of lanthanoid nitrates with 18-crown-6 (18-c-6) and tetrahalocatecholate (X_4Cat^{2-}, X=Cl, Br) ligands has afforded two compound series $[Ln(18\text{-}c\text{-}6)(X_4Cat)(NO_3)]\cdot MeCN$ (X=Cl, **1-Ln**; X=Br, **2-Ln**; Ln=La, Ce, Nd, Gd, Tb, Dy). The analogues of both series with Ln=Ce, Nd, Tb and Dy exhibit slow magnetization relaxation at low temperature. Concerted magnetic measurements, EPR spectroscopy, and *ab initio* calculations on magnetically diluted and undiluted samples have allowed the elucidation of the mechanisms responsible for slow magnetic relaxation. This comprehensive investigation suggested that the spin dynamics are governed by Raman processes at higher temperatures, transitioning to a dominant phonon bottleneck process as the temperature is decreased, with an observed T^{-6} rather than the usual T^{-2} dependence (T being the temperature). This anomalous thermal dependence of the phonon bottleneck relaxation is consistent with anharmonic effects in the lattice dynamics, which was predicted by Van Vleck more than 70 years ago

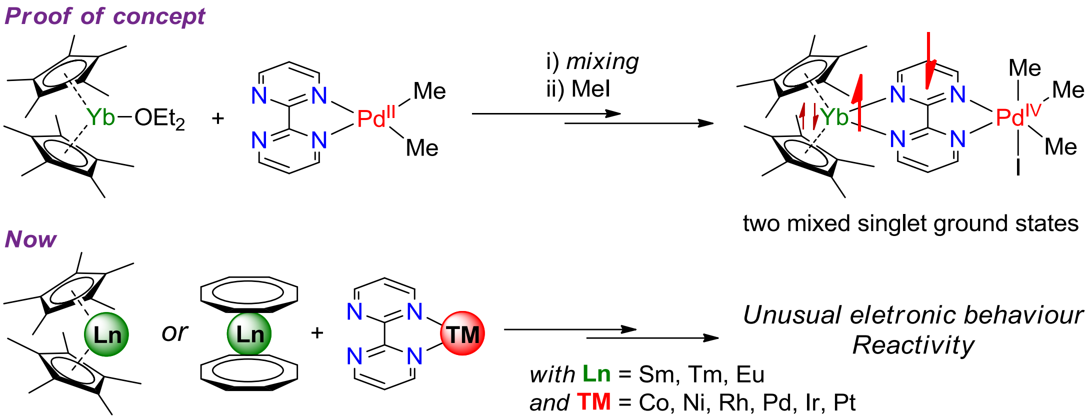
Heterobimetallic complexes with transition metals and lanthanides: Modulation of the electronic properties

Jules Moutet,[a] Poonam Singh,[a] Jules Schleinitz,[a] Ding, Wang,[a] Maxime Tricoire,[a] Valeriu Cemortan,[a] Marie Cordier,[a] Grégory Nocton[a]

[a] LCM, Ecole polytechnique, CNRS, Université Paris-Saclay, Route de Saclay, 91128, Palaiseau cedex, France.
e-mail : jules.moutet@polytechnique.edu

Since 1965, various divalent lanthanide complexes have been developed[1] and display a specific ability to easily transfer one electron.[2] In association with redox non-innocent ligands, this approach could promote a renewed reactivity of transition metal centers.[3] In addition, this would lead to new transition metal complexes whose electronic structure would have distinctive features.

Our group has recently released an original heterobimetallic system containing an ytterbium organolanthanide as electron source and a palladium center with bipyrimidine redox-active ligand (Figure 3).[4] This induces an electronic behavior that is described with a multiconfigurational ground state,[5,6] and allows the stabilization of high-valent Pd^{IV} complex. From now on, we are interested in more reductive divalent lanthanide[7] centers (such as Sm^{II} and Tm^{II}) and their effect on redox-active structures coordinated with group 9 and 10 transition metals (Figure 3). We expect unusual electronic configuration that could lead to slow magnetic relaxation behavior or unsuspected reactivity.



with **Ln** = Sm, Tm, Eu
and **TM** = Co, Ni, Rh, Pd, Ir, Pt

Figure 3

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[1] Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1965**, *3*, 181-187.
[2] G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen *J. Am. Chem. Soc.* **2014**, *136*, 8626-8641.
[3] Chirik, P. J.; Wieghardt, K. *Science,* **2010**, *327*, 794-795.
[4] V. Goudy, A. Jaoul, M. Cordier, C. Clavaguéra, G. Nocton *J. Am. Chem. Soc.* **2017**, *139*, 10633-10636.
[5] C. H. Booth, M. D. Walter, D. Kazhdan, Y. Hu, W. W. Lukens, E. D. Bauer, L. Maron, O. Eisenstein, R. A. Andersen *J. Am. Chem. Soc.* **2009**, *131*, 6480-6491.
[6] C. H. Booth, D. Kazhdan, E. L. Werkema, M. D. Walter, W. W. Lukens, E. D. Bauer, Y. Hu, L. Maron, O. Eisenstein, M. Head-Gordon, R. A. Andersen *J. Am. Chem. Soc.* **2010**, *132* , 17537-17549.
[7] L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryan *J. Phys. Chem.* **1973**, *77*, 1528-1539.

An original recycling method for Li-ion batteries by producing MOFs in large scale

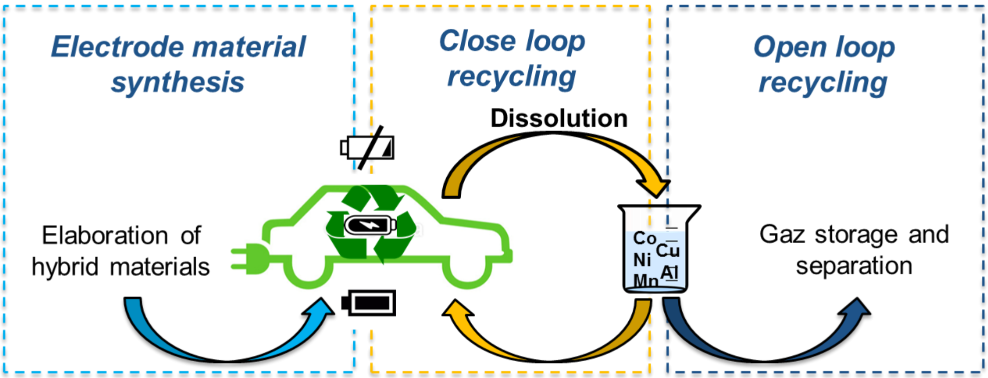
Marine Cognet, Julien Cambedouzou, Michael Carboni, Daniel Meyer

ICSM, CEA/UM/CNRS/ENSCM, Bagnols-sur-Ceze, France
e-mail : michael.carboni@cea.fr

Energy storage is one of the biggest challenges for next decades. The management of renewable energy production requires efficient electrochemical energy storage devices to use it anytime and anywhere. In recent years, Li-ion batteries (LiBs) have been developed and successfully commercialized for portable devices (smartphones, laptops ...) or cars. Current recycling processes are not well enough developed or economically interesting and only 50% of actual LIBs in weight are recycled due to the law (Directive EU 2006/66/CE) hinders a sustainable development.

A mixture of cobalt/nickel/manganese has been largely used in the development of the LiB (NMC batteries). Our team has recently proposed a closed loop recycling process by selective precipitations of these toxic metals as valuable materials [1] (Metal organic Frameworks (MOFs)). MOFs, due to their high surfaces and tunable structures, have been used in many applications as gas storage, heterogeneous catalysis, metals separation or even as electrode materials [2].

A CoNiMn MOF obtained from simulant battery waste solution has been tested as electrode in a coin cell. It has revealed capacities as high as 460 mAh/g with a good cyclability over 50 charge/discharge cycles. Our recent studies have been focused on adapting this strategy by using real LiB wastes. It has been possible to obtain in large scale from LiB wastes some known MOFs reported for their ability for gas storage. This strategy can create an economical open loop recycling process to develop valuable materials from wastes.



[1] E. Perez, R. Navarro Amador, M. Carboni, D. Meyer, *Materials Letters*, **2016**, *167*, 188-191.
[2] M. Cognet, T. Gutel, D. Peralta, J. Maynadie, M. Carboni, D. Meyer, *J. of The Electrochemical Society*, **2017**, *164*, 12, A2552-A2554.

Complexes poly-nucléaires à base d'ions Mn^{2+} et de macrocycles thiacalix[4]arène : synthèses et propriétés optiques

Constance Lecourt,[a] Dominique Luneau,[a] Cédric Desroches[a]

[a] *Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Laboratoire des Multimatériaux et Interfaces, F-69622 Villeurbanne*
e-mail : constance.lecourt@univ-lyon1.fr

Les macrocycles de type thiacalix[4]arènes[1], dérivés des calixarènes, comportent quatre groupements phénoliques reliés entre eux par des atomes de soufre. La possibilité d'oxyder[2] ces atomes de soufre en sulfinyl (ThiaSO) ou sulfonyl ($ThiaSO_2$), renforce d'autant plus le fort pourvoir chélatant du ligand macrocyclique, engendré par la proximité des phénoxydes. Sa capacité à former des clusters poly-nucléaires, ainsi que ses propriétés électroniques, en font un ligand de choix pour aboutir à des systèmes moléculaires à propriétés optique et/ou magnétiques.

Par synthèse solvothermale et en présence d'une base telles que KF ou KOH (fig.1), dans le méthanol, nous avons obtenu les clusters tétranucléaires[3] de Mn^{2+} suivants : $K[Mn_4(ThiaSO_2)_2OH]$ et $K[Mn_4(ThiaSO_2)_2F]$. Les quatre ions métalliques, bloqués entre deux macrocycles, sont co-planaires et emprisonnent en leur centre un anion pontant de type μ^4-OH^- ou μ^4-F^-, procurant une charge négative aux complexes.

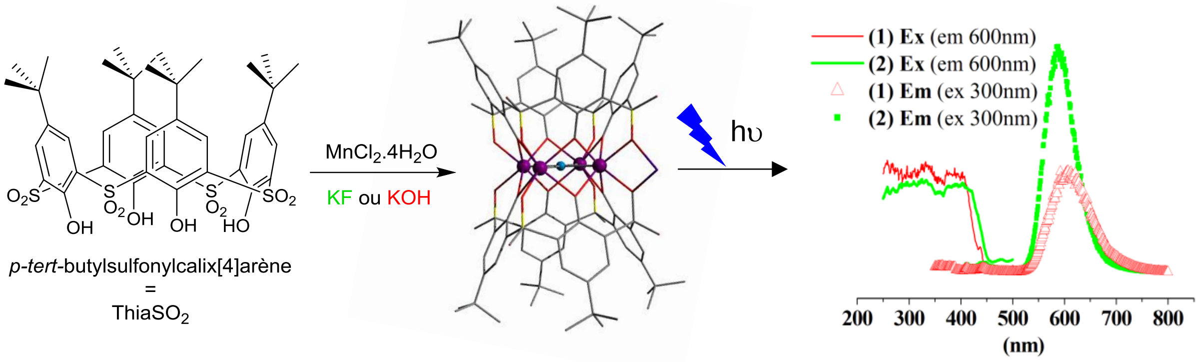


Figure 1 : Synthèse, structure et propriétés optiques des complexes $K[Mn_4(ThiaSO_2)_2OH]$ et $K[Mn_4(ThiaSO_2)_2F]$

L'originalité de ces composés est d'une part structurale, avec la coordination du manganèse peu commune en bi-prisme trigonal capé, et d'autre part optique. Sous irradiation UV (hυ< 400 nm), ces complexes présentent une forte luminescence, avec une longueur d'onde d'émission aux alentours de 600 nm. Cette luminescence a été attribuée à la transition $^4T_1 \rightarrow {}^6A_1$ de l'ion Mn^{2+}, rendue possible par l'effet d'antenne du ligand.

Afin d'améliorer et de moduler les propriétés optiques de cette famille de complexes, nous avons entrepris des modifications chimiques du ligand. Notre but est, par exemple, d'augmenter la délocalisation d'électrons au sein du macrocycle et ainsi déplacer la bande d'absorption vers le domaine de longueurs d'onde du visible.

La synthèse et les propriétés optiques de ces nouveaux complexes seront présentées lors de cette communication.

[1] H. Kumagai *et al.*, tetrahedron lett., **1997**, 38, 3971
[2] N. Iki *et al.*, tetrahedron lett., **1998**, 41, 7559
[3] C. Desroches *et al.*, dalton trans., **2012**, 41, 2707

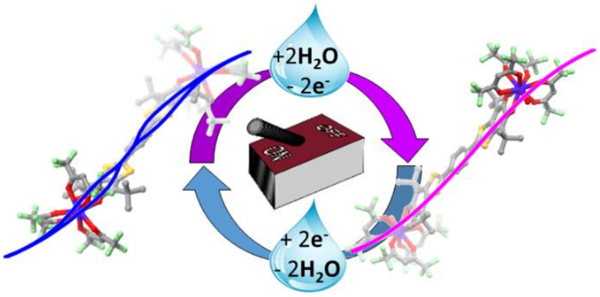
Redox- and Hydro-Magnetic Switching in Lanthanide-Based Single-Molecule Magnets

Fabrice Pointillart,[a] Jessica Flores Gonzalez,[a] Vincent Montigaud,[a] Olivier Cador,[a]
Boris Le Guennic,[a] Lahcène Ouahab,[a] Viacheslav Kuropatov[b]

[a] *Institut des Sciences Chimiques de Rennes UMR 6226 CNRS-UR1, Université de Rennes 1, 35042 Rennes Cedex, France.* [b] *G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, 603950, GSP-445, Trpinina str., 49, Nizhny Novgorod, Russia.*

e-mail :fabrice.pointillart@univ-rennes1.fr

The Single-Molecule Magnets (SMMs)[1] fascinated both chemist and physicist communities for the last three decades because of their potential applications in high-density data storage, Quantum computing and Spintronics.[2] Even more challenging is the design of multi-properties SMMs, especially when the switching of one of these properties can be controlled. Such behavior could be open additional applications for switches and sensors but has been rarely achieved in the litterature.[3] In this presentation, the study of the dinuclear complex $[Dy_2(hfac)_6(HSQ\text{-}L)]\cdot CH_2Cl_2$ (**HSQ-Dy**) (where hfac = 1,1,1,5,5,5-hexafluoroacethylacetonate and HSQ-L = 2,2'-benzene-1,4-diylbis(6-hydroxy-4,7-di-tert-butyl-1,3-benzodithiol-2-ylium-5-olate)[4] is presented.[5] The complex can be reversibly oxidized into the dinuclear compound $[Dy_2(hfac)_6(H_2O)_2(Q\text{-}L)]$ (**Q-Dy**) (where Q-L = 2,2'-cyclohexa-2,5-diene-1,4-diylidenebis(4,7-di-tert-butyl-1,3-benzodithiole-5,6-dione)) inducing coordination of water molecule to the Dy^{III} ion and its release. **HSQ-Dy** is a Single-Molecule Magnet with a magnetic relaxation 7000 times slower than for **Q-Dy** (at 3 K) allowing an "ON-OFF" switch of the magnetic bistability. In other words, the first simultaneous redox and hydro-magnetic switching was achieved. The modulation of the magnetic anisotropy in **HSQ-Dy** and **Q-Dy** was quantified by ab initio calculations.



Hydro- and redox-switching of the magnetic bistability in the $[Dy_2(hfac)_6(HSQ\text{-}L)]\cdot CH_2Cl_2$ dinuclear complex

[1] R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804.
[2] S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, *Science* **2014**, *344*, 1135.
[3] I.-R. Jeon, L. Sun, B. Negru, R. P. Van Duyne, M. Dinca, T. David Harris, *J. Am. Chem. Soc.* **2016**, *138*, 6583-6590.
[4] N. O. Chalkov, V. K. Cherkasov, G. A. Abakumov, G. V. Romanenko, S. Y. Ketkov, I. V. Smolyaninov, A. G. Starikov, V. A. Kuropatov, *Eur. J. Org. Chem.* **2014**, 4571-4576.
[5] F. Pointillart, J. Flores Gonzalez, V. Montigaud, S. Norkov, B. Le Guennic, O. Cador, L. Ouahab, V. Kuropatov, *manuscript under preparation*

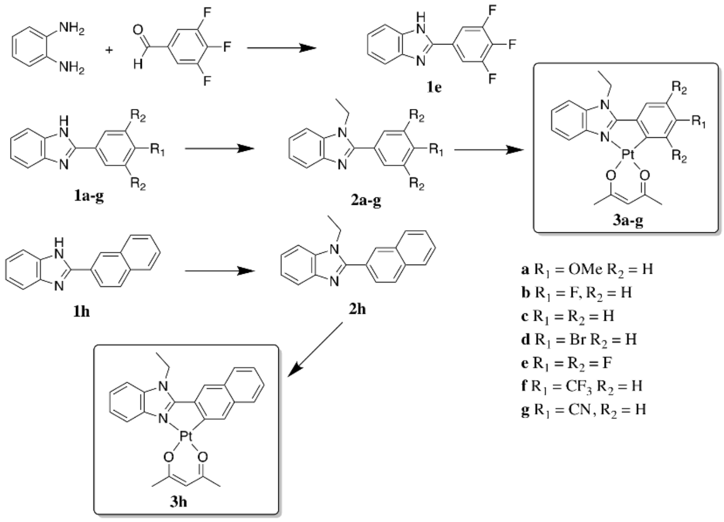
Neutral Heteroleptic Cyclometallated Platinum(II) Complexes Featuring 2-Phenylbenzimidazole Ligand as Bright Emitters in Solid State and in Solution.

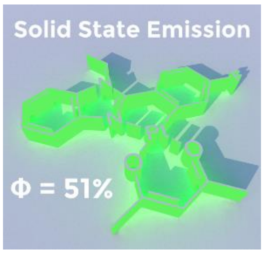
Pierre-Henri Lanoë,[a] Angelica Moreno-Betancourt, [a] Laura Wilson, [a] Christian Philouze, [a] Cyrille Monnereau, [b] Hélène Jamet, [a] Damien Jouvenot [a] and Frédérique Loiseau [a]

[a] *Département de Chimie Moléculaire, Université Grenoble Alpes, UMR-5250 CNRS UGA, CS 40700, 38058 Grenoble Cedex 9, France*

[b] *Univ Lyon, Ens de Lyon, CNRS UMR 5182, Université Lyon 1, Laboratoire de Chimie, F69342, Lyon, France*
e-mail : pierre-henri.lanoe@univ-grenoble-alpes.fr, frederique.loiseau@univ-grenoble-alpes.fr

A series of 8 neutral cyclometallated platinum(II) complexes featuring 2-phenylbenzimidazole chromophoric ligand and acetylacetonate as ancillary ligand has been synthesized and characterized. The introduction of a variety of substituent on the phenyl ring allows to finely tune the emission wavelength. The emission data reveal high quantum yield in deaerated solution and in bulk solid state (micro-crystalline powder), with values up to an impressive 51%. The emission for all of the complexes is attributed to a mixed 3LC-MLCT state. Both absorption and emission data have been correlated successfully with the redox potentials and the Hammett parameters.





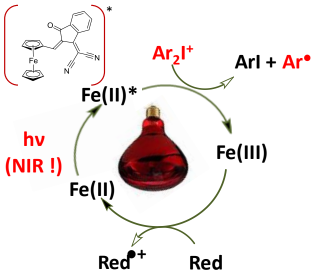
Ferrocenes as (photo)redox catalysts for polymerization under visible to NIR lights

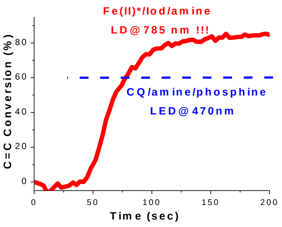
Guillaume Noirbent,[a] Patxi Garra,[b,c] Damien Brunel,[a] Jacques Lalevée,[b,c] Didier Gigmes,[a] Frédéric Dumur,[a]

[a] Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France. [b] Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse. [c] Université de Strasbourg, France
e-mail : Guillaume.noirbent@outlook.fr

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 ferrocenes as photocatalysts will be presented. Precisely, the mechanisms of photooxidation reaction of Fe(II) in presence of an iodonium salt – leading to a reaction between the excited state of the ferrocenes and the iodonium salt (Fe(II)*/Ar_2I^+) and applied to the highly challenging field of photopolymerization will be detailed. The access to filled and thick samples thanks to NIR photopolymerization will also be discussed.[1]





[1]. P. Garra, D. Brunel, G. Noirbent, B. Graff, F. Morlet-Savary, C. Dietlin, V. F. Sidorkin, F. Dumur, D. Duché, D. Gigmes, J.-P. Fouassier, J. Lalevée, manuscript under submission (2019).

Electron transfer in a covalent dye–cobalt catalyst assembly – a transient absorption spectroelectrochemistry perspective

Murielle Chavarot-Kerlidou,[a] Sebastian Bold,[a,b,c] Julien Massin,[a] Maximilian Bräutigam,[b,c] Maria Wächtler,[b,c] Vincent Artero,[a] Benjamin Dietzek.[b,c]

[a]Laboratoire de Chimie et Biologie des Métaux, Univ. Grenoble Alpes, CNRS, CEA, 38000 Grenoble, France. [b]Friedrich Schiller University, Jena, Germany. [c]Leibniz Institute of Photonic Technology Jena (IPHT), Jena, Germany

e-mail : murielle.chavarot-kerlidou@cea.fr, www.solhycat.com

The development of photoelectrochemical devices for water splitting is highly demanded to directly convert solar energy into chemical energy, under the form of a “solar fuel” such as hydrogen H_2. A promising strategy, inspired from dye-sensitized solar cells, relies on the covalent grafting of molecular photosensibilisateur-catalyst assemblies onto a suitable electrode material.[1] Our group developed a functional H_2-evolving dye-sensitized photocathode by immobilizing the noble metal-free dyad **2** (Fig. 1a) onto mesoporous NiO films.[1] In such dyads, understanding the excited state dynamics and electron transfer mechanisms is important for rationally improving the molecular assembly design. Excited state processes and electron transfer were investigated for **2** and for the reference dye **1** by time-resolved spectroscopy. In order to access all oxidation states of the cobalt catalyst unit – from Co(III) to Co (I), a novel transient absorption spectroelectrochemistry (TA-SEC) set-up was built (Fig. 1b). The resulting study established that, for dyad **2** in solution, oxidative quenching of the dye excited state by the cobalt center does not take place.[2] Furthermore, the dye unit **1** was immobilized onto NiO and transient absorption spectroscopy allowed to get insights on hole injection kinetics and charge-separated state lifetimes.[3]

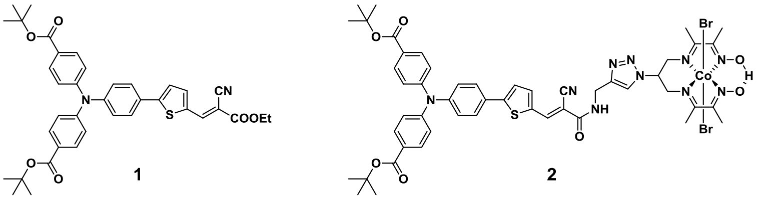


Figure 1a – Reference dye 1 and dye-catalyst assembly 2

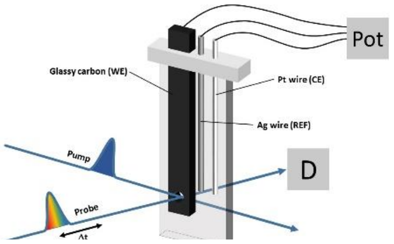


Figure 4b - Cell for TA-SEC measurements

[1]. P. Xu, N. S. McCool, T. E. Mallouk *Nano Today*, **2017**, *14*, 42-58.

[2]. N. Kaeffer, J. Massin, C. Lebrun, O. Renault, M. Chavarot-Kerlidou, V. Artero *J. Am. Chem. Soc.* **2016**, *138*, 12308-12311.

[3]. S. Bold, L. Zedler, Y. Zhang, J. Massin, V. Artero, M. Chavarot-Kerlidou, B. Dietzek *Chem. Commun.* **2018**, *54*, 10594-10597.

[4]. J. Massin, M. Bräutigam, S. Bold, M. Wächtler, A. B. Muñoz-García, M. Pavone, B. Dietzek, M. Chavarot-Kerlidou, V. Artero; *submitted for publication*.

Manganese-carbonyl complexes as catalysts for CO_2 electrochemical reduction

Matthew Stanbury, Jean-Daniel Compain, Monica Trejo, Parker Smith, Eric Gouré,
Sylvie Chardon-Noblat

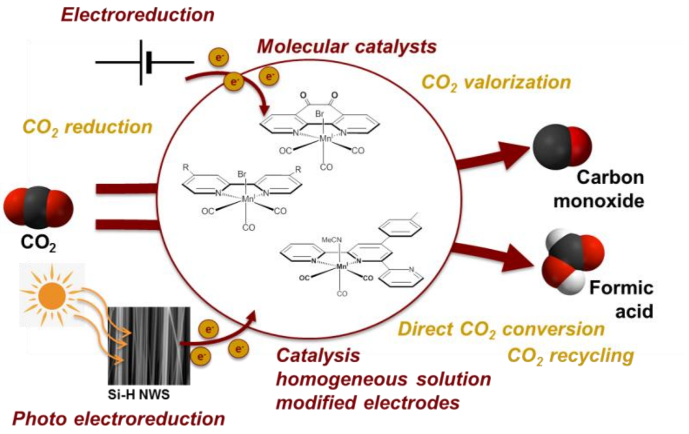
Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France
e-mail : sylvie.chardon@univ-grenoble-alpes.fr

Carbon dioxide conversion is increasingly gaining attention as CO_2 is increasingly being regarded as a feedstock for the preparation of a wide range of value added commodities such as useful chemical raw materials or energy rich products. However, an efficient CO_2 transformation process is challenging, but it has great potential for the demand of future resources that do not rely on petrochemical sources.

The CO_2 reduction reaction requires high-yield, an input of energy and a catalyst. It can be performed on molecular catalysts. Among various experimental techniques that can be implemented, electrocatalytic CO_2 Reduction Reactions (ECO_2RR) have promise as they convert electrical energy into chemicals (energy storage). In the past thirty years, several transition metal complexes, able to convert CO_2 by ECO_2RR, have been studied. This includes systems based on Re, Ru and Os bipyridyl carbonyl systems, however, very few earth abundant efficient metal based molecular catalysts have been reported so far.

Much of our present work[1] is focussed on developing and studying new Mn-based catalysts and understanding their CO_2 reduction catalytic properties with ECO_2RR pathway, in order to gain a better understanding with the aim to improving and advancing this field of CO_2 transformation.

Therefore here we will present our on-going research which is helping to better understand ligand effects on the CO_2 catalytic reduction processes and especially the important role that ligand can have on catalytic activity and therefore efficiency and product selectivity, yield and overall catalyst stability under catalytic conditions.



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[1] (a) M. Bourrez, F. Molton, S. Chardon-Noblat, A. Deronzier, *Angew. Chem. Int. Ed.* **2011**, *50*, 9903; (b) E. Torralba-Penalver, Y. Luo, J.-D. Compain, S. Chardon-Noblat, B. Fabre, *ACS Catal.* **2015**, *5*, 6138; (c) J.-D. Compain, M. Stanbury, M. Trejo and S. Chardon-Noblat, *Eur. J. Inorg. Chem.* **2015**, 5757; (d) M. Stanbury, J.-D. Compain, M. Trejo, P. Smith, E. Gouré, S. Chardon-Noblat, *Electrochim. Acta* **2017**, *240*, 288; (e) M. Stanbury, J.-D. Compain, S. Chardon-Noblat, *Coord. Chem. Rev.* **2018**, *361*, 210.

Mechanosynthesis: Green Chemistry applied to the design of copper-based photoinitiators

Frédéric Dumur,[a] Mariem Bouzratti-Zerelli,[b,c] Guillaume Noirbent,[a] Jacques Lalevée,[b,c] Didier Gigmes,[a]

[a] Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France. [b] Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse. [c] Université de Strasbourg, France
e-mail : Guillaume.noirbent@outlook.fr

Photoinitiated polymerization plays a more and more important role in industry as reflected by the continuously growing number of applications of this technique in conventional areas such as coatings, inks, and adhesives but also in high-tech domains, like optoelectronics, laser imaging, stereolithography and nanotechnology. Indeed, photopolymerization presents several advantages such as very short reaction time even at room temperature and the absence of solvents avoiding the formation of volatile organic compounds (VOC). Moreover, the possibility to irradiate with high precision specific zones allows the spatial-control of the polymerization.[1] Since 2011, photoinitiating systems able to initiate polymerization under soft light irradiation sources have been the subject of intense efforts to minimize the risks and the costs related to the conventional UV irradiation. However, even if some results are promising, so far the reported systems still present low to moderate reactivity and can hardly compete with actual UV systems.

In the search for new photoinitiating systems, copper (II) complexes have been identified as promising candidates for the development of photoinitiating systems usable in industrial processes for coating applications (cationic polymerization of epoxide-based resins), the manufacture of Interpenetrating Polymer Networks (IPNs) (polymerization of acrylate/epoxy blends) and the production of thick epoxy/glass fiber composites. The development of photocatalytic systems was also possible with copper complexes so that a reduced content (30 fold less compared to the BAPO content) could still lead to higher practical efficiencies than than that obtained with BAPO in the photopolymerization of coatings.

Parallel to high photoinitiating efficiencies, the mechanosynthesis of copper complexes has been identified as a promising approach for the design of photoinitiators. Comparison of the performances obtained for the photopolymerization of epoxides and acrylates for photoinitiators obtained by mechanosynthesis or by classical chemistry in solution revealed the polymerization abilities to be comparable.

In this presentation, a comparison with other reference systems based on 2-isopropylthioxanthone or anthracene is also provided and outlines again the very high performance of copper complexes for industrial applications. The development of photoredox catalysts based on copper complexes provides a means for creating photoinitiating systems with unprecedented reactivity. Currently, no photoredox catalysts exist on the market and the design of photoinitiators by mechanosynthesis is not under use in industry yet.

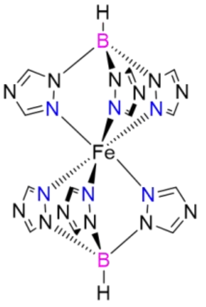
[1]. H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Polym. Chem. 8, 5580–5592 (2017).

Spin crossover molecular layer on substrate: study of its formation and its use for an optical application

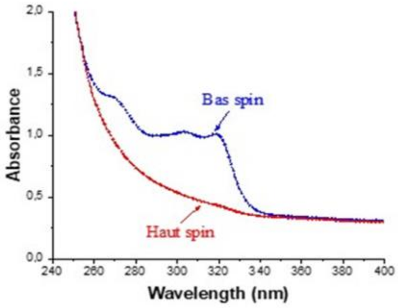
Lucie Routaboul[a], Alin-Ciprian Bas [a,b], Victoria Shalabaeva[a], Xavier Thompson,[a]
Laure Vendier [a], Lionel Salmon [a], Christophe Thibault [b], Gábor Molnár [a], and
Azzedine Bousseksou[a]

[a] LCC-CNRS, Université de Toulouse, CNRS, 31077 Toulouse, France
[b]LAAS-CNRS, Université de Toulouse, CNRS, INSA, 31077 Toulouse, France
e-mail : lucie.routaboul@lcc-toulouse.fr

We have recently been extensively investigating the molecular spin crossover compound [$Fe^{II}(HB(tz)_3)_2$] (tz = 1,2,4-triazol-1-yl) (**1**).[1,2,3,4] It is characterized by an isostructural and abrupt first-order spin transition between its LS and HS configurations, near room temperature (*ca.* 333 K), with a narrow thermal hysteresis loop (*ca.* 2 K width). Moreover, this compound is one rare example of sublimable spin cross-over complexes, therefore SCO materials of complex **1** can be prepared by evaporation on a substrate. These films can potentially be used for optical applications since molecular layers of **1** are homogeneous, crystalline and with a very high purity and tight thickness control.[5] The complex in the low spin (LS) state has significantly different chemical and physical properties from the complex in the high spin (HS) state. If we focus on the optical properties, the complex in LS state absorbs much more in UV than the complex in HS state. We should stress that a crystalline film has a much larger Δ_{Abs} than an amorphous one. This presentation discusses the formation of molecular films of SCO on glass substrates, as well as the use of the large Δ_{Abs} in an optical application.



Complex **1**



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[1] Rat, S., K. Ridier, L. Vendier, G. Molnar, L. Salmon, and A. Bousseksou, *CrystEngComm* 2017, 19: 3271-80.

[2] Shalabaeva, Victoria, Mirko Mikolasek, Maria D. Manrique-Juarez, Alin-Ciprian Bas, Sylvain Rat, Lionel Salmon, William Nicolazzi, Gabor Molnar, and Azzedine Bousseksou, *J. Phys. Chem. C* 2017, 121: 25617-21.

[3] Manrique-Juarez, Maria D., Fabrice Mathieu, Victoria Shalabaeva, Jean Cacheux, Sylvain Rat, Liviu Nicu, Thierry Leichle, Lionel Salmon, Gabor Molnar, and Azzedine Bousseksou, *Angew. Chem., Int. Ed.* 2017 56: 8074-78.

[4] Shalabaeva, Victoria, Karl Ridier, Sylvain Rat, Maria D. Manrique-Juarez, Lionel Salmon, Isabelle Seguy, Aurelian Rotaru, Gabor Molnar, and Azzedine Bousseksou. *Appl. Phys. Lett.* 2018, 112: 013301/1-01/5.

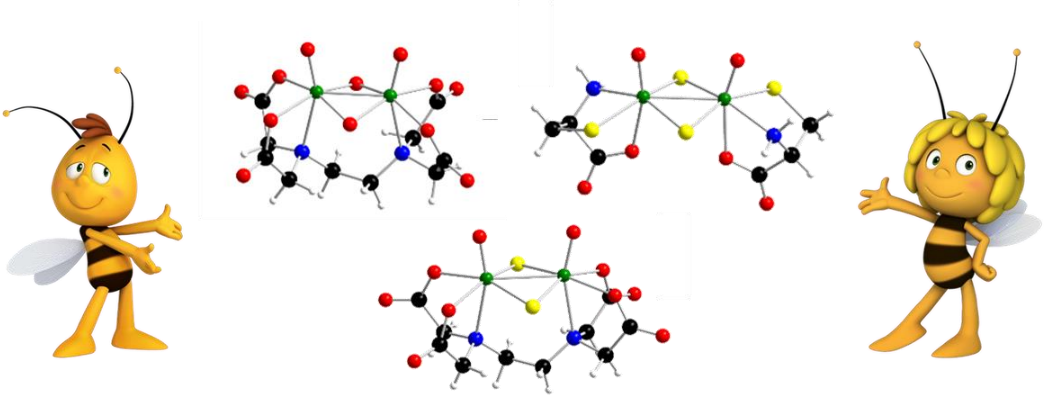
[5] Shalabaeva, Victoria, Sylvain Rat, Maria Dolores Manrique-Juarez, Alin-Ciprian Bas, Laure Vendier, Lionel Salmon, Gabor Molnar, and Azzedine Bousseksou, *J. Mater. Chem. C.* 2017, 5: 4419-25.

$[Mo_2O_2S_2]^{2+}$-based coordination chemistry: from synthesis to environmental applications

Arcadie Fuior,[a,b] Sébastien Floquet,[a] Valentina Cebotari,[c] Ion Toderas,[c]
Aurelian Gulea,[b] Emmanuel Cadot.[a]

[a] *Institut Lavoisier of Versailles, University of Versailles, University Paris-Saclay, 45 avenue des Etats-Unis, 78035 Versailles, France.*
[b] *Institut de Zoologie de l'Académie des Sciences de Moldavie, Chisinau, Moldavie,*
[c]*Université d'Etat de Moldavie, Chisinau, Moldavie.*
e-mail : sebastien.floquet@uvsq.fr;

In recent decades, the chemistry of polyoxometalates has experienced very strong growth due to their diversity and their applications in many fields. Consisting mostly of molybdenum or tungsten in their highest oxidation state, the introduction of sulfur in the chemistry of polyoxometalates stabilizes lower oxidation degrees and provides greater versatility in systems formed. To achieve this, one possible way is to use preformed molybdic fragments as the building block $[Mo_2O_2S_2]^{2+}$. During this presentation, I would endeavor to illustrate the richness of the supramolecular chemistry we can develop with this small molecular cluster. [1-3] In a first part, I would give an overview of $[Mo_2O_2S_2]$-based chemical systems we obtained in Versailles, before focusing on very surprising environmental applications we can get with very simple coordination complexes based on this cluster.[4]



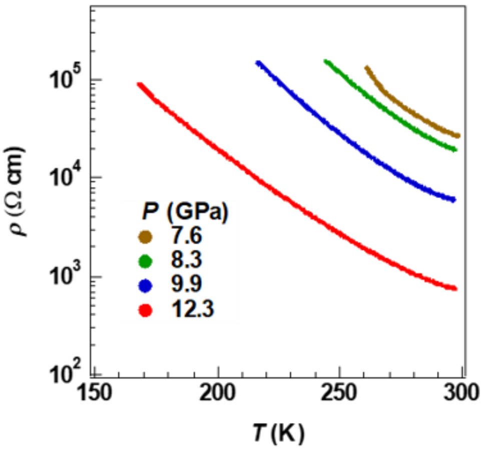
[1]. E. Cadot, M.N. Sokolov, V.P. Fedin, C. Simonnet-Jégat, S. Floquet, F. Sécheresse, *Chem. Soc. Rev.*, **2012**, 7335-7353.
[2]. J.-F. Lemonnier, S. Duval, S. Floquet and E. Cadot. *Isr. J. Chem.*, 2011, 51, 290-302.
[3] A. Hijazi, J.C. Kemmegne-Mbouguen, S. Floquet, J. Marrot, J. Fize, V. Artero, O. David, E. Magnier, B. Pégot, E. Cadot, *Dalton trans*., **2013**, 42, 4848-4858.
[4] S. Floquet, E. Cadot, A. Hijazi, A. Gulea, V. Tapcov, V. Bulimaga, L. Zosim. Patent N° 4319 MD, MD - BOPI 1/**2015** p33; " I. Toderas, A. Gulea, V. Cebotari, S. Floquet, E. Cadot, I. Buzu. MD - BOPI 4/**2016** p16.

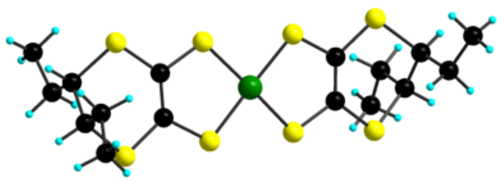
Molecular conductors based on chiral metal-bis(dithiolene) complexes: structures and transport properties under very high pressure

Alexandre Abhervé[a], Flavia Pop[a], HengBo Cui[b], Reizo Kato[b], Narcis Avarvari[a].

[a] Laboratoire MOLTECH-Anjou, 2 Boulevard Lavoisier, 49045 Angers, France
[b] Condensed Molecular Materials Laboratory, RIKEN, Wako-shi, Saitama 351-0198, Japan
e-mail : alexandre.abherve@univ-angers.fr

Metal-bis(dithiolene) complexes are an important family of molecular conductors since they usually have a small HOMO-LUMO energy gap and can thus present a metallic band structure under pressure. Recently, we have reported the first examples of chiral single-component molecular conductors of formula [M(dm-dddt)$_2$] (M = Au, Ni; dm-dddt = 5,6-dimethyl-5,6-dihydro-1,4-dithiin-2,3-dithiolate).[1] Transport measurements on single crystals of both (*S*,*S*,*S*,*S*) and (*R*,*R*,*R*,*R*) enantiomers indicated a semiconducting behaviour of the open-shell gold complexes and activation energies strongly influenced by hydrostatic pressure.
In the last years, resistivity measurements under very high pressure could be performed using a diamond anvil cell (DAC). It has shown the appearance of metal-like behaviours in molecular semiconductors[2] and the emergence of the Dirac electron system in the single-component molecular conductor [Pd(dddt)$_2$].[3]
To get new insights on the mechanism of conductivity in single-component molecular conductors, and to study the effects of chirality on the transport properties, we designed a series of chiral metal-bis(dithiolene) complexes and performed resistivity measurements under very high pressure.





[1]. D. G. Branzea, F. Pop, P. Auban-Senzier, R. Clérac, P. Alemany, E. Canadell, N. Avarvari, *J. Am. Chem. Soc.* **2016**, *138*, 6838-6851.
[2] H. Cui, J. S. Brooks, A. Kobayashi, K. Kobayashi, *J. Am. Chem. Soc.* **2009**, *131*, 6358-6359.
[3] R. Kato, H. Cui, T. Tsumuraya, T. Miyazaki, Y. Suzumura, *J. Am. Chem. Soc.* **2017**, *139*, 1770-1773.

A nickel-NHC complex as an efficient pre-catalyst for the selective Markovnikov or *anti*-Markovnikov hydroboration of styrenes

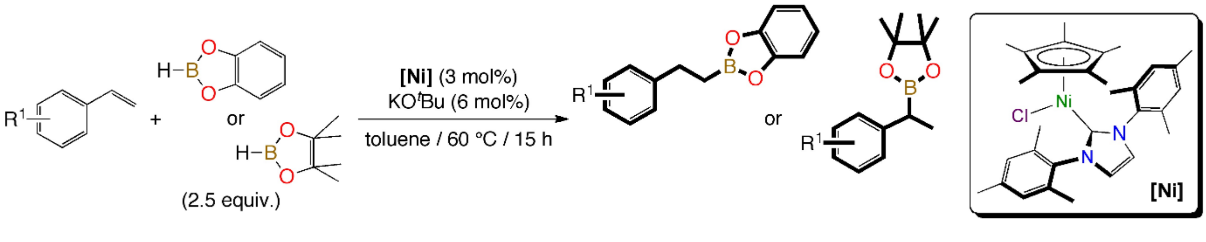
Franck Ulm,[a] Michael J. Chetcuti,[a] Jean-Pierre Djukic,[b] Vincent Ritleng[a]

[a] *Université de Strasbourg, Laboratoire d'Innovation Moléculaire et Applications, UMR CNRS 7042, 25 rue Becquerel, 67087 Strasbourg.* [b] *Université de Strasbourg, Institut de Chimie, UMR CNRS 7177, 4 rue Blaise Pascal, 67070 Strasbourg*
e-mail : vritleng@unistra.fr

Boronic acid and ester derivatives are very important starting materials in molecular synthesis. Among the practical methods for their preparation, the hydroboration of alkenes is of great interest since (i) alkenes constitute a readily available feedstock and (ii) it is one the most straightforward and atom-thrifty synthetic routes to create new C–B bonds.[1] The main drawback of this methodology is that it is principally based on noble metals, such as rhodium and iridium, which declining natural reserves make the quest for alternatives with less expensive and more sustainable earth-abundant metals desirable.

Recent work has seen the emergence of 1st row transition metals, most notably manganese, iron, cobalt and copper.[2] In contrast, despite its intrinsic fascinating reactivity which has led to a renaissance of its chemistry,[3] nickel has barely been used for this transformation. There are indeed only a couple of examples with narrow reaction scopes and practically no mechanistic information.[4]

In this context, we reported a few years ago that air-stable nickel-NHC complexes of the type $[\mathrm{Ni^{II}Cp^{\dagger}(NHC)L}]^{(+)}$ ($\mathrm{Cp^{\dagger}}$ = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5), L = Cl^- or NCMe) behave as efficient pre-catalysts for the hydrosilylation of aldehydes, ketones and imines.[5] This initial entry into hydro-functionalization reactions has now allowed us to establish that the readily available [NiCp*(IMes)Cl] complex efficiently catalyses the hydroboration of styrenes in the presence of a catalytic amount of potassium *tert*-butoxide.[2b] Depending on the nature of the borane, the reaction is either Markovnikov or *anti*-Markovnikov selective, and tolerates both electron-withdrawing and -donating groups on styrene derivatives (Scheme 1). A combination of ^{1}H and ^{11}B NMR spectroscopic studies, radical-trap experiments, cyclic voltammetry measurements, fuel cell experiments and piezometric measurements provides insight to the reaction mechanism.



[1]. G. C. Fu, *Transition Metal-Catalyzed Hydroboration of Olefins*, In *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals.* Ed. M. Beller, C. Bolm, 2nd Ed., Wiley-VCH: Weinheim, 2008.
[2]. (a) S. C. Schmid, R. Van Hoveln, J. W. Rigoli, J. M. Schomaker, *Organometallics* **2015**, *34*, 4164. (b) J. H. Docherty, J. Peng, A. P. Dominey, S. P. Thomas, *Nature Chem.* **2017**, *9*, 595.
[3]. S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* **2014**, *509*, 299.
[4] (a) E. E. Touney, R. Van Hoveln, C. T. Buttke, M. D. Freidberg, I. A. Guzei, J. F. Schomaker, *Organometallics* **2016**, *35*, 3436. (b) S. Pereira, M. Srebnik, *Tetrahedron Lett.* **1996**, *37*, 3283.
[5]. (a) L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J.-B. Sortais, V. Ritleng, *Adv. Synth. Catal.* **2012**, *354*, 2619. (b) L. P. Bheeter, M. Henrion, M. J. Chetcuti, C. Darcel, V. Ritleng, J.-B. Sortais, *Catal. Sci. Technol.* **2013**, *3*, 3111.

Nanovecteurs multifonctionnels à base de MIL-100(Fe) comme nouvelle plateforme pour la théranostique

Saad Sene, [a,b] Nicolas Menguy, [c] Sylvain Miraux, [d] Florence Gazeau, [e] Christian Serre, [a] Nathalie Steunou. [f]

[a] Institut des Matériaux Poreux de Paris, FRE 2000 CNRS, Ecole Normale Supérieure, Ecole Supérieure de Physique et des Chimie Industrielles de Paris, PSL Research University, 75005 Paris, France.
[b] Institut Charles Gerhardt, Equipe Ingénierie Moléculaire et Nano-Objets, Université de Montpellier, CNRS, ENSCM, Place Eugène Bataillon, 34095, Montpellier, Cedex 5,France
[c] Institut de Minéralogie de Physique des Matériaux et de Cosmochimie, UMR CNRS 7590, UPMC Univ Paris 06, 75252 Paris cedex 05, France.
[d] Centre de Résonance Magnétique des Systèmes Biologiques, UMR CNRS 5536, Université Bordeaux-2, 33076 Bordeaux Cedex.
[e] Laboratoire Matière et Systèmes Complexes (MSC), UMR CNRS 7057, Université Paris Diderot, Bât. Condorcet, 10 rue A. Domon et L. Duquet, 75013 Paris, France.
[e] Institut Lavoisier, UMR CNRS 8180, UVSQ, 78035 Versailles Cedex. Université Paris-Saclay, France.
E-mail: saad.sene@umontpellier.fr

Le développement continu des nanotechnologies a conduit à des innovations intéressantes dans le domaine de la médecine. Pour le traitement du cancer par exemple, l'utilisation des nanoparticules biocompatibles permet d'avoir des systèmes de libération de principes actifs plus efficaces ou des agents de contraste plus performants pour de l'imagerie. Les récents progrès permettent également de combiner ces deux propriétés au sein d'un même nanovecteur, permettant ainsi de faire de la théranostique. [1]

Récemment, de nouveaux matériaux hybrides biodégradables, les Metal Organic Frameworks (MOFs), sont apparus comme des matériaux prometteurs pour des applications biomédicales. [2] Ces matériaux structurés et hautement poreux sont construits à partir de sous-unités inorganiques et de ligands polytopiques organiques. De par leur structure et diversité chimique, il en résulte des propriétés intéressantes pour la biomédecine dont une grande capacité d'encapsulation de principes actifs, une dégradabilité et une biocompatibilité. [3]

Dans le but de développer un nanovecteur multifonctionnel pouvant être utilisé pour la théranostique, le trimésate de fer mésoporeux (MIL-100(Fe)) a été associé à des oxydes de fer superparamagnétiques (USPIO) γFe_2O_3 utilisés comme agents de contraste. Avec une approche simple exploitant la charge de surface des NPs, les oxydes de fer ont été adsorbés à la surface du MIL-100(Fe) pour préparer les composites. Les caractérisations effectuées montrent d'intéressantes propriétés dont une bonne stabilité colloïdale, une capacité d'encapsulation et de libération de principes actifs préservée, et de bonnes valeurs de relaxivité. De plus, des études in vitro complémentaires montrent une faible toxicité des composites mais également leur activité antitumorale après encapsulation d'une molécule anticancéreuse, la doxorubicine, tandis que des expériences in vivo démontrent leur efficacité comme agents de contraste pour l'IRM. Toutes ces propriétés attestent donc du potentiel prometteur du composite MIL-100(Fe)-USPIO comme nanovecteur bimodal couplant des propriétés de thérapie et d'imagerie. [4]

[1] L. Eun-Kyung et al., *Chem. Rev*. **2015**, *115*, 327.
[2] P. Horcajada et al., *Chem. Rev.* **2012**, *112*, 327.
[3] P. Horcajada et al., *Nat. Mat.* **2010**, *9*, 172.
[4] S. Sene et al., *Chem*. **2017**, *3*, 303.

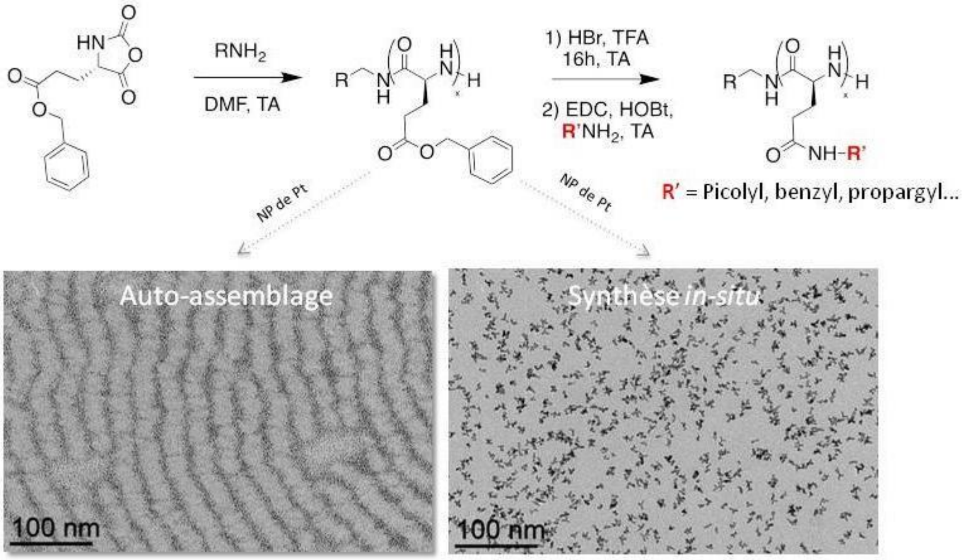
Matériaux hybrides nanostructurés à base de nanoparticules de platine et de polymères peptidiques

Ghada Manai,[ab] Hend Houimel[a] Bruno Chaudret,[a] Simon Tricard,[a] Colin Bonduelle[b]

a LPCNO (Laboratoire de Physique et Chimie des Nano-Objets), INSA, CNRS, Université de Toulouse,135 Avenue de Rangueil, 31077 Toulouse
b LCC (Laboratoire de Chimie de Coordination), CNRS, Université de Toulouse, 205 route de Narbonne, F-31077 Toulouse.
E-mail: manai@insa-toulouse.fr

Mots-clés: polypeptides, nanoparticules métalliques, chimie de coordination, autoassemblage.

Les polypeptides sont des macromolécules synthétiques constituées d'acides aminés. Le développement de leurs méthodologies de synthèse a facilité leurs intégrations et leurs utilisations extensives dans différents domaines à l'interface avec les sciences du vivant. [1]
Les polypeptides sont d'intérêt majeur car ils apportent une structuration biomimétiques et parfois une 'bioactivité' spécifique. Cette structuration est contrôlée par les fonctions portées par les chaines latérales du polymère: ces dernières sont critiques et permettent d'élaborer des matériaux dont la structuration supramoléculaires serait difficile à obtenir avec des polymères non peptidiques.[2] Ce travail présente la synthèse de poly(γ-benzyl-L-glutamate) (PBLG) via la polymérisation par ouverture de cycle de γ- benzyl-L-glutamate N-carboxyanhydride ainsi que la modulation des fonctions portées par ses chaînes latérales. Cette modulation met en œuvre deux étapes de synthèse post-polymérisation: une hydrolyse et un couplage peptidique activé par des carbodiimides. Les fonctions introduites ont pour but d'interagir avec la surface de nanoparticules métalliques et de finalement aboutir à la préparation de nano-composites intelligents (électricité, déformation mécanique). Cette synthèse de nanocomposites peut se faire en mélangeant des polypeptides avec des nanoparticules préformées (auto-assemblage) ou en utilisant ces polymères comme matrice pendant la synthèse de nanoparticules (synthèse in-situ).



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[1] T. J. Deming, *Nat. Mater*., **2010**, 9, 535.
[2] H. Dong, J. Y. Shu, N. Dube, Y. F. Ma, M. V. Tirrell, K. H. Downing and T. Xu, *J. Am. Chem. Soc*., **2012**, 134, 11807.

Synthesis of copper nanoparticles with tunable sizes and shapes

Liyan Ouyang,[a] Emmanuel Vrancken,[a] Armelle Ouali,[a] Alexa Courty,[b] Hélène Gerard[c]

[a] Institut Charles Gerhardt UMR 5253 CNRS-UM-ENSCM,240 Avenue du Professeur Emile Jeanbrau ,34296 Montpellier Cedex 5, France.
[b] Sorbonne Université, UPMC Univ Paris 06,UMR 8233, Laboratoire MONARIS,F-75005 Paris, France
[c] Laboratoire de Chimie Théorique, UMR 7616, UPMC-Université Paris 06,CNRS case 137, 4 Place Jussieu, 75262 Paris Cedex 05, France.

e-mail : liyan.ouyang@enscm.fr

In the past decades, the metallic nanoparticles (NPs) have found numerous applications in nanomedicine, catalysis and imaging due to their interesting physical properties (optical, electrical, thermal).[1-2] It is now well established that their shape and size play a very important role in determining their properties.[3] It has also been shown that the morphology of various metallic NPs can be tuned through the control of the synthesis conditions and the nature of the ligands used. Among NPs of the 11th group, copper NPs has received less attention despite their lower cost compared to silver or gold due to their poor air-stability.[4]
We are currently studying the synthesis of copper nanocubes with controlled size distribution through a simple disproportionation reaction approach in organic solvent.[5] Depending on synthesis conditions, Cu nanocubes with good size-distribution and with relative air-stability compared to Cu nanospheres have been obtained.

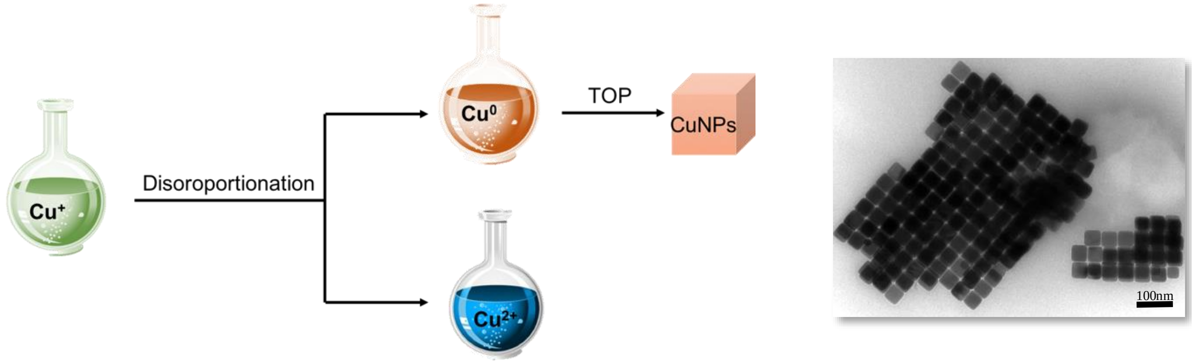

Figure 1. Synthesis of Cu nanocubes via a simple disproportionation reaction approach

[1]. D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem. Int. Ed*. **2005**, *44*, 7852.
[2]. N. N. Hoover, B. J. Auten, B. D. Chandler, *J. Phys. Chem. B.* **2006**, *110*, 8606-8612.
[3]. Y. Xia, Y. J. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed*. **2009**, *48*, 60-103.
[4]. M. A. B. Aissa, B.Tremblay, A. Andrieux-Ledier, E. Maisonhaute, N. Raouafi and A.Courty, *Nanoscale.* **2015**, *7*, 3189-3195.
[5]. H. Guo, Y. Chen, M.B. Cortie, X. Liu, Q. Xie, X.Xiang, D. Peng, *J. Phys. Chem. C.* **2014**, *118(18),* 9801-9808.

Multinuclear solid state NMR investigations of the structure of metal complexes, coordination polymers and functionalized NPs

Christel Gervais,[a] Christian Bonhomme,[a] Saad Sene,[b] Marie-Alix Pizzocaro,[b]
Philippe Gaveau,[a] Thomas-Xavier Métro,[d] Dorothée Berthomieu,[a]
Danielle Laurencin[a]

[a] Sorbonne Université, UPMC Univ Paris 06,UMR 7574, LCMCP, F-75005 Paris, France
[b] Institut Charles Gerhardt, UMR 5253 CNRS-UM-ENSCM, Pl. E. Bataillon, 34095 Montpellier France.
[c] Current adress: Universidad de La Rioja, Logroño, Spain
[d] Institut des Biomolécules Max Mousseron, UMR 5247, CNRS-UM-ENSCM, Pl. E. Bataillon, CC 34095 Montpellier Cedex 5, France.
e-mail : danielle.laurencin@umontpellier.fr

Current multinuclear solid state NMR approaches are uniquely suited for studying the structure of a variety of compounds involving coordination bonds, such as metal complexes, coordination polymers, and grafted nanoparticles.[1] Here, we will illustrate how high resolution solid state NMR can be used to gain detailed insight into the mode of binding between organic ligands and metal centers:

- either by analyzing the ligands themselves by NMR. Here, this will be exemplified in the case of coordination networks and functionalized nanoparticles involving organoboron ligands (Figure 1).[2,3]
- or by studying the metal centers directly. NMR analyses of metal complexes and coordination polymers based on alkaline earth metals (^{25}Mg, ^{43}Ca, ^{87}Sr and ^{137}Ba) will be shown to illustrate this.[2,4]

Our recent developments aiming at making oxygen-17 a more common probe for NMR will also be presented, through the development of novel enrichment schemes based on mechanochemistry.[5]

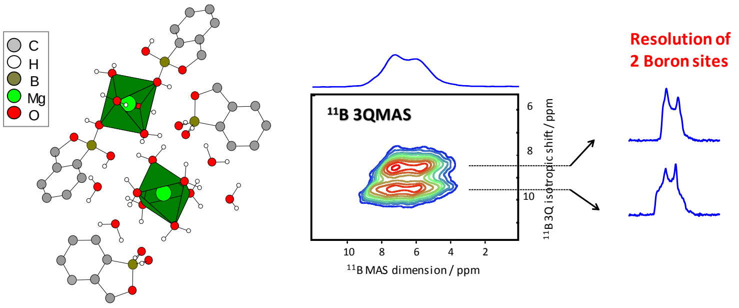

Figure 1. ^{11}B MQMAS NMR spectrum of a Mg-benzoxaborolate complex (9.4 T, 20 kHz MAS).2

[1] a) B. E. G. Lucier , S. Chen, Y. Huang, *Acc. Chem. Res.* **2018**, *51*, 319; b) A. Marchetti, J. Chen, Z. Pang, S. Li, D. Ling, F. Deng, X. Kong, *Adv. Mater.* **2017**, *29*, 1605895; c) C. Bonhomme, C. Gervais, D. Laurencin, *Prog. Nucl. Magn. Reson. Spectrosc.* **2014**, *77*, 1-48.
[2] S. Sene, S. Begu , C. Gervais , G. Renaudin , A. Mesbah , M. E. Smith , P. H. Mutin , A. van der Lee , J.-M. Nedelec , C. Bonhomme , D. Laurencin, *Chem. Mater.* **2015**, *27*, 1242-1254;
[3] M.-A. Pizzoccaro, O. Nikel, S. Sene, C. Philippe, P. H. Mutin, S. Bégu, D. Vashishth, D. Laurencin, *Acta Biomater.* **2016**, *41*, 342-350.
[4] a) S. Sene, B. Bouchevreau, C. Martineau, C. Gervais, C. Bonhomme, P. Gaveau, F. Mauri, S. Bégu, P. H. Mutin, M. E. Smith, D. Laurencin, *CrystEngComm*, **2013**, *15*, 8763-8775; b) Sene, M.-A. Pizzoccaro, J. Vezzani, M. Reinholdt, P. Gaveau, D. Berthomieu, S. Bégu, C. Gervais, C. Bonhomme, G. Renaudin, A. Van Der Lee, A. Mesbah, M. E. Smith, D. Laurencin, *Crystals*, **2016**, *6*, 48.
[5] T.-X. Métro, C. Gervais, A. Martinez, C. Bonhomme, D. Laurencin, *Angew. Chem.* **2017**, *56*, 6803-6807. The European Research Council (ERC) is acknowledged for funding this work (grant No. 156605).

Liste des Participants

Liste des Participants

Nom	Prénom	Affiliation	E-mail
Abed Ali Abdine	Racha	ENSCM - ICGM	racha.abed-ali-abdine@enscm.fr
Abhervé	Alexandre	Université d'Angers	alexandre.abherve@univ-angers.fr
Amgoune	Abderrahmane	Université Lyon 1	abderrahmane.amgoune@univ-lyon1.fr
Arous	Omar	USTHB	omararous@yahoo.fr
Aukauloo	Ally	Université Paris Sud	ally.aukauloo@u-psud.fr
Avarvari	Narcis	Université d'Angers	narcis.avarvari@univ-angers.fr
Bantreil	Xavier	Université de Montpellier - IBMM	xavier.bantreil@umontpellier.fr
Bastin	Stéphanie	CNRS - LCC	stephanie.bastin@lcc-toulouse.fr
Bechu	Damien	Université de Strasbourg	damien.bechu@etu.unistra.fr
Bellemin-Laponnaz	Stéphane	IPCMS	stephane.bellemin@ipcms.unistra.fr
Benzai	Amal	Rennes 1	amal.benzai@etudiant.univ-rennes1.fr
Beranger	Michel	Interchim	interchim.sud@interchim.fr
Berthet	Jean-Claude	CEA Saclay	jean-claude.berthet@cea.fr
Bienvenu	Geert	Agilent Technologies	geert.bienvenu@non.agilent.com
Bontemps	Sébastien	CNRS - LCC	bontemps@lcc-toulouse.fr
Boudiaf	Djoumana	Université d'Alger	boudiafdjoumana@gmail.com
Brunel	Damien	Aix-Marseille Université	damien.brunel@univ-amu.fr
Cahu	Maëlle	Université de Montpellier - ICGM	maelle.cahu@etu.umontpellier.fr
Canac	Yves	CNRS - LCC	yves.canac@lcc-toulouse.fr
Carboni	Michael	CEA - Marcoule	michael.carboni@cea.fr
Cebotari	Diana	Université de Versailles	cebotaridiana1995@gmail.com
César	Vincent	CNRS - LCC	vincent.cesar@lcc-toulouse.fr
Chardon	Sylvie	Université Grenoble Alpes	sylvie.chardon@univ-grenoble-alpes.fr
Chavarot-Kerlidou	Murielle	Université Grenoble Alpes	murielle.chavarot-kerlidou@cea.fr
Chebbi	Mohamed Rami	ENSCM - ICGM	mohamed-rami.chebbi@enscm.fr
Clément	Sébastien	Université de Montpellier - ICGM	sebastien.clement1@umontpellier.fr
Clot	Eric	CNRS - ICGM	eric.clot@umontpellier.fr
Colacino	Evelina	Université de Montpellier - ICGM	evelina.colacino@umontpellier.fr
Delavaux-Nicot	Béatrice	CNRS - LCC	beatrice.delavaux-nicot@lcc-toulouse.fr
Djedouani	Amel		djedouani_amel@yahoo.fr
Donat	Jordan	CEA Grenoble	jordan.donat@cea.fr
Drobek	Martin	CNRS - IEM	martin.drobek@umontpellier.fr
Dumur	Frédéric	Institut de Chimie Radicalaire	frederic.dumur@univ-amu.fr
Durand	Jean-Olivier	CNRS - ICGM	durand@um2.fr
Efremova	Tzvetelina	Université Montpellier - ICGM	tzvetelina.efremova@umontpellier.fr
Esmieu	Charlène	CNRS - LCC	charlene.esmieu@lcc-toulouse.fr
Evrard	Quentin	INSA	quentin.evrard@insa-rennes.fr
Fateeva	Alexandra	Université de Lyon 1	alexandra.fateeva@univ-lyon1.fr
Felix	Gautier	CNRS - ICGM	gautier.felix@umontpellier.fr
Fellak	Somia	Faculté des Sciences et Techniques de Fès	soumaya.fellak@gmail.com
Floquet	Sébastien	Université de Versailles	sebastien.floquet@uvsq.fr

Fuior	Arcadie	Université de Versailles	arcadie.fuior@uvsq.fr
Gernet	Aurélie	ENSCM - ICGM	aurelie.gernet@enscm.fr
Giannoudis	Emmanouil	Université Grenoble Alpes	emmanouil.giannoudis@cea.fr
Glatz	Jana	Sorbonne Université	jana.glatz@sorbonne-universite.fr
Goeb	Sébastien	Université d'Angers - MOLTECH-Anjou	sebastien.goeb@univ-angers.fr
Gorra	Melvyn	Université Montpellier	gorramelvyn@yahoo.fr
Guari	Yannick	CNRS - ICGM	yannick.guari@umontpellier.fr
Guillaumont	Maya	Sorbonne Université	mguillaumont@yahoo.com
Hesemann	Peter	CNRS - ICGM	peter.hesemann@umontpellier.fr
Houamria	Hamza	Faculté de Médecine Annaba	hamzapharm2000@yahoo.fr
Ivanov	Anton	Université de Versailles	ivanov338@niic.nsc.ru
Izzet	Guillaume	Sorbonne Université	guillaume.izzet@sorbonne-universite.fr
Jaroschik	Florian	CNRS - ICGM	florian.jaroschik@enscm.fr
Kahn	Myrtil	CNRS - LCC	myrtil.kahn@lcc-toulouse.fr
Kosinska	Aneta	ENSCM - ICGM	kosinskaneta@wp.pl
Labande	Agnès	CNRS - LCC	agnes.labande@lcc-toulouse.fr
Lamaty	Frédéric	CNRS - IBMM	frederic.lamaty@umontpellier.fr
Lanoë	Pierre-Henri	Université Grenoble Alpes	pierre-henri.lanoe@univ-grenoble-alpes.fr
Larionova	Joulia	Université de Montpellier - ICGM	joulia.larionova@umontpellier.fr
Laurencin	Danielle	CNRS - ICGM	danielle.laurencin@umontpellier.fr
Leclerc	Nathalie	Université de Versailles	nathalie.leclerc@uvsq.fr
Lecourt	Constance	Université Claude Bernard Lyon 1	constance.lecourt@univ-lyon1.fr
Lemercier	Gilles	Reims Champagne-Ardenne	gilles.lemercier@univ-reims.fr
Lemouzy	Sébastien	ENSCM - ICGM	sebastien.lemouzy@enscm.fr
Long	Jérôme	Université de Montpellier - ICGM	jerome.long@umontpellier.fr
Lorignon	Fabrice	CEA Marcoule	lorignon@gmail.com
Louvain	Nicolas	Université de Montpellier - ICGM	nicolas.louvain@umontpellier.fr
Luneau	Dominique	Université Claude Bernard Lyon 1	dominique.luneau@univ-lyon1.fr
Luttringer	Florian	Université de Montpellier - IBMM	florian.luttringer@etu.unistra.fr
Mamontova	Ekaterina	Université de Montpellier - ICGM	ekaterina.mamontova@umontpellier.fr
Manai	Ghada	INSA Toulouse	manai@insa-toulouse.fr
Mathonière	Corine	Université de Bordeaux - ICMCB	Corine.Mathoniere@icmcb.cnrs.fr
Mejia	Angelica	Université Toulouse III Paul Sabatier	angelica.mejia.f@gmail.com
Monge	Miguel	Uiversidad de La Rioja	miguel.monge@unirioja.es
Monnier	Florian	ENSCM - ICGM	florian.monnier@enscm.fr
Mouchfiq	Ahmed	Collège de France	ahmed.mouchfiq@college-de-france.fr
Moutet	Jules	Ecole Polytechnique	jules.moutet@gmail.com
Nebel	Eric	Agilent Technologies	eric.nebel@agilent.com
Nierengarten	Jean-François	Université de Strasbourg - CNRS	nierengarten@unistra.fr
Noirbent	Guillaume	Institut de Chimie Radicalaire	guillaume.noirbent@outlook.fr
Norbert-Agaisse	Eliott	Université de Montpellier - ICGM	eliott.norbert-agaisse@umontpellier
Ohleier	Alexia	CEA Saclay	alexia.ohleier@cea.fr
Ouali	Armelle	CNRS - ICGM	armelle.ouali@enscm.fr
Ouyang	LiYan	ENSCM - ICGM	liyan.ouyang@enscm.fr
Perier	Caroline	Agilent Technologies	caroline.perier@agilent.com
Peris	Eduardo	Universitat Jaume I	eperis@qio.uji.es

Perrot	Claire	Agilent Technologies	claire.perrot@agilent.com
Pointillart	Fabrice	Université de Rennes 1	fabrice.pointillart@univ-rennes1.fr
Poirot	Alexandre	Université Paul Sabatier	poirot@chimie.ups-tlse.fr
Poli	Rinaldo	CNRS - LCC	rinaldo.poli@lcc-toulouse.fr
Policar	Clotilde	Ecole Normale Supérieure	clotilde.policar@ens.fr
Prioleau	Céline	Interchim	celine.prioleau@interchim.com
Proust	Anna	Sorbonne Université	anna.proust@sorbonne-universite.fr
Quintin	François	Université de Montpellier - IBMM	francois.quintin@umontpellier.fr
Raehm	Laurence	Université de Montpellier	laurence.raehm@umontpellier.fr
Reinaud	Olivia	Université Paris Descartes	olivia.reinaud@parisdescartes.fr
Rezkallah	Fatima	Université de Montpellier - ICGM	fatima.rezkallah@umontpellier.fr
Richeter	Sébastien	Université de Montpellier - ICGM	sebastien.richeter@umontpellier.fr
Ritleng	Vincent	Université de Strasbourg	vritleng@unistra.fr
Rivada Wheelaghan	Orestes	Université Paris Diderot	orestes.rivada@gmail.com
Rodríguez Castillo	María	Université de La Rioja	rodriguezcastillo.ma@gmail.com
Rose	Clémence	Université de Montpellier - ICGM	clemence.rose@etu.umontpellier.fr
Rousset	Elodie	Université de Reims Champagne Ardenne	elodie.rousset@univ-reims.fr
Routaboul	Lucie	CNRS - LCC	lucie.routaboul@lcc-toulouse.fr
Salvalaio	Véronique	Editions Dunod	vsalvalaio@dunod.com
Sene	Saad	Université de Montpellier - ICGM	saad.sene@umontpellier.fr
Shore	Andrew	Royal Society of Chemistry	shorea@rsc.org
Sortais	Jean-Baptiste	LCC- Université Paul Sabatier	jean-baptiste.sortais@lcc-toulouse.fr
Taillefer	Marc	CNRS - ICGM	marc.taillefer@enscm.fr
Tanchoux	Nathalie	CNRS - ICGM	nathalie.tanchoux@enscm.fr
Thieuleux	Chloé	CNRS - CPE Lyon	thieuleux@cpe.fr
Ulm	Franck	Université de Strasbourg	franck.ulm@etu.unistra.fr
Voyron	Sébastien	Jasco France	svoyron@jascofrance.fr
Vranken	Emmanuel	ENSCM - ICGM	emmanuel.vrancken@enscm.fr
Wang	Ding	Ecole Polytechnique	ding.wang@polytechnique.edu
Zaid	Yassir	ENSCM - ICGM	yassir.zaid@enscm.fr
Zerkani	Hannou	Université Moulay Ismail	hannouzerkani@gmail.com
Zhang	Dan	LCC-CNRS	dan.zhang@lcc-toulouse.fr