10ème Journée Scientifique du LabEx

CHARMMAT
LABEX
CHIMIE DES ARCHITECTURES MOLÉCULAIRES MULTIFONCTIONNELLES ET DES MATÉRIAUX

1er et 2 décembre 2022

Amphithéâtre de l'I2BC du campus CNRS,

Avenue de la terrasse
91190 Gif-sur-Yvette

Conférenciers Invités

Dr. M.A. FERNANDES, University of Amsterdam – Pays Bas

"S,O-Ligand-promoted Pd-catalyzed C−H Functionalization Reactions."

Pr P. ANDREAZZA, Université d'Orléans

"Equilibrium and metastable behaviour of multi-metallic supported nanoparticles investigated by X-ray Scattering"

Pr. T. KAWAI, NAIST – Japon

"Synergetic Approaches for Highly Sensitive Photoreactive Systems"

Pr A. SMITH, University of St Andrews - Ecosse

"Catalytic Enantioselective [2,3]- and [1,2]-rearrangements of allylic ammonium ylides and ethers"

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Dr M. KAHN, LCC Toulouse

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

Dr A. QUADRELLI, IRCE Lyon

"ALD Growth of ultrathin films and mechanistic insight by surface organometallic chemistry"

Dr A. BRUNELLE, LAMS Paris

"Fine and complex organic-inorganic layers in old paintings revealed by TOF-SIMS mass spectrometry imaging"

Le programme inclut des communications orales présentées par des jeunes chercheurs et des post-doctorants financés par le LabEx, ainsi qu'une séance de communications par affiche.

Comité d'Organisation :
H. Amy, G. Clavier, J. P. Mahy, N. Jarroux, A. Voituriez, J. Xie

BIENVENUE A TOUS

PROGRAMME

Planning journées Charmmmat - 1er décembre 2022			
8h30 ACCUEIL			
9h00	Mot d'accueil	J.-P. MAHY	CHARMMMAT 2011-2022
9h45	Conférencier 45 mn	M.A. FERNANDES	S,O-Ligand-promoted Pd-catalyzed C–H Functionalization Reactions.
10h30	Chercheur Charmmmat 25 mn	A. CLARAZ	An electrochemical approach towards the synthesis of fluorine-containing compounds
10h55	Post-doctorant 15 mn	E. PRADAYROL	
11h10-11h30	Pause-café - séance de posters		
11h30	Chercheur Charmmmat 25 mn	J.-N. REBILLY	Electro-Assisted Oxidation of Thioanisole by an "O2 Activator/Oxidizing Species
11h55	Post-doctorant 15 mn	N. ZEAITER	
12h10 - 14H00	Déjeuner – séance de posters		
14h00	Conférencier 45 mn	P. ANDREAZZA	Equilibrium and metastable behaviour of multi-metallic supported nanoparticles investigated by X-ray Scattering
14h45	Chercheur Charmmmat 25 mn	M.-P. GAIGEOT	Developments in algorithmic graph theory, supervised learning and game theory for theoretical chemistry
15h10	Post-doctorant 15 mn	A. NOUAILLE	Synthesis and characterization of new anion receptors
15h25 - 16h00	Pause-café - séance de posters		
16h00	Conférencier 45 mn	T. KAWAI	Synergetic Approaches for Highly Sensitive Photoreactive Systems
16h45	Chercheur Charmmmat 25 mn	S. CACOVICH	Multidimensional Photoluminescence Analysis for Photovoltaic Materials and Devices
17h10	Post-doctorant 15 mn	J. ARI	Laser polarization-controlled crystallization and orientation of nonlinear optical nanocrystals in multicomponent glasses using a femtosecond laser for photonic applications
17h30	Fin de la 1ère journée		

Planning journées charmmmat - 2 décembre 2022

8h30	Accueil		
9h00	Conférencier 45 mn	A. SMITH	Catalytic Enantioselective [2,3]- and [1,2]-rearrangements of allylic ammonium ylides and ethers
9H45	Chercheur Charmmmat 25 mn	A. DE LA TORRE	Copper Catalysis-Enabled Enantioselective Cycloadditions
10H10	Post-doctorant 15 mn	E. DAIANN SOSA CARRIZO	Switching the selectivity in the Rh(II) Catalyzed C(sp3)-H amination of propylbenzene: insights from a DFT viewpoint
10h25 - 10h45	Pause-café - séance de posters		
10h45	Conférencier 45 mn	M. KAHN	Synthesis of metal oxide nanoparticles by organometallic approach: from molecule to devices
11h30	Chercheur Charmmmat 25 mn	L. CALVET	Integrating smart sensors and materials into bio-inspried hardware
11h55	Post-doctorant 15 mn	J. PHAM	Electrofluorochromism of surface-confined BODIPYs
12h10 - 13h30	Déjeuner – séance de posters		
13H30 - 14H15	Conférencier 45 mn	A. QUADRELLI	ALD Growth of ultrathin films and mechanistic insight by surface organometallic chemistry
14H15 - 14H40	Chercheur Charmmmat 25 mn	C. SICARD	Mesoporous Metal-Organic Frameworks for the encapsulation of Microperoxidase-8 and other bio-entities
14H40 - 15H00	Pause-café - séance de posters		
15H00 - 15H45	Conférencier 45 mn	A. BRUNELLE	Fine and complex organic-inorganic layers in old paintings revealed by TOF-SIMS mass spectrometry imaging
15H45 - 16H10	Chercheur Charmmmat 25 mn	R. MEALLET	Luminescent Organic Nanoparticles as tools for biological or health issues
16h10 - 16h25	Post-doctorant 15 mn	M. BAYAT	Comprehensive structural assignment of glycosaminoglycans by aerolysin nanopore
16h30	J.-P. MAHY		Conclusion

CONFERENCIERE

M. Ángeles (Tati) FERNANDES IBANEZ

S,O-Ligand-promoted Pd-catalyzed C−H Functionalization Reactions

M. Ángeles (Tati) Fernández-Ibáñez

Van 't Hoff Institute for Molecular Sciences, Faculty of Science, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
m.a.fernandezibanez@uva.nl

Metal-catalyzed C−H functionalization has become a powerful synthetic tool to introduce complexity in organic molecules since no pre-functionalization of starting materials is required, reducing the number of synthetic steps, the cost of the process and the waste formation, all key aspects for the development of sustainable synthetic routes. However, the low reactivity and selectivity observed in many of these processes hamper the broad implementation of this strategy in organic laboratories. To unlock the full potential of metal-catalyzed C-H functionalization, the discovery of new ligands capable of increasing the reactivity and controlling the selectivity is of central importance.[1]

In this communication, I will present the discovery and development of new type of S,Oligands capable of promoting a variety of C−H functionalization reactions in a highly selective manner.[2]

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[2] (a) Naksomboon, K.; Valderas, C.; Gómez-Martínez, M.; Álvarez-Casao, Y.; Fernández-Ibáñez, M. Á. *ACS Catal*. **2017**, 7, 6342; (b) Álvarez-Casao, Y.; Fernández-Ibáñez, M. Á. *Eur. J. Org. Chem*. **2019**, 1842. (c) Naksomboon, K.; Poater, J.; Bickelhaupt, F. M.; Fernández-Ibáñez, M. A. *J. Am. Chem. Soc*. **2019**, *141*, 6719. (d) Jia, W.-L.; Westerveld, N.; Wong, K. M.; Morsch, T.; Hakkennes, M.; Naksomboon, K.; Fernández-Ibáñez, M. Á. *Org. Lett*. **2019**, *21*, 9339. (e) Jia, W. -L.; Vega Ces S.; Fernández-Ibáñez M. A. *J. Org. Chem*. **2021**, *86*, 6259. (f) Sukowski, V.; Jia, W.-L.; van Diest, R.; van Borselen, M.; Fernández-Ibáñez, M. A. *Eur. J. Org. Chem*. **2021**, *29*, 4132. (g) Deng, K.-Z.; Jia, W.-L.; Fernández-Ibáñez, M. A. *Chem. Eur. J*.**2021**, e202104107. (h) Sukowski, V.; van Borselen, M.; Mathew, S.; Fernández-Ibáñez, M. A. *Angew. Chem. Int. Ed*. **2022**, e202201750

Aurélie CLARAZ

An electrochemical approach towards the synthesis of fluorine-containing compounds.

A. Claraz

Institut de Chimie des Substances Naturelles, CNRS, Univ. Paris-Saclay, 1 Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France

aurelie.claraz@cnrs.fr

Thanks to the unique properties of the fluorine atom, fluorine-containing organic compounds have found significant applications in pharmaceuticals, agrochemicals and material sciences.[1] Therefore, there is constantly a strong need for the development of novel and mild synthetic methodologies to access such molecules.

Radical-based transformations are attractive complementary strategies to traditional ionic reactions. In this regard, the desire to improve the sustainability of organic processes and to explore novel modes of reactivity has spawned a renewal of interest for organic electrochemistry to generate radical species.[2] Considering these advantages, we decided to launch a program directed towards the electrochemical synthesis of fluorine-containing molecules. Herein, we disclose the electrooxidative trifluoromethylation of allylamines leading to various 5- and 6-membered CF_3-containing azacycles and the preparation of *gem*-difluoroalkenes through electroreductive couplings.[3]

[1] (a) D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308. (b) K. Müller, C. Faeh and F. Diederich, *Science*, **2007**, *317*, 1881. (c) M. Inoue, Y. Sumii and N. Shibata, *ACS Omega*, **2020**, *5*, 10633. (d) Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai and N. Shibata, *iScience*, **2020**, *23*, 101467.

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Jean-Noël REBILLY

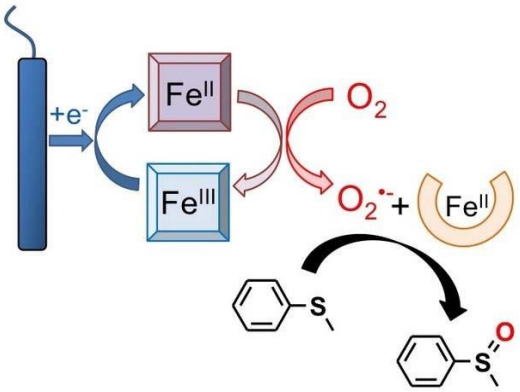
Electro-Assisted Oxidation of Thioanisole by an "O2 Activator/Oxidizing Species" Tandem System of Non-Heme Iron Complexes

Amanda Lyn Robinson, Jean-Noël Rebilly, Régis Guillot, Christian Herrero, Hélène Maisonneuve, Frédéric Banse

Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris-Saclay, 17 Av. des Sciences, 91400 Orsay

jean-noel.rebilly@universite-paris-saclay.f

Oxidation reactions play a crucial role in the synthesis of synthons used in a variety of domains. For instance, epoxides are used in the polymer industry.[1-2] Their synthesis often involves O_2 as an oxidant, but due to its triplet state, reactions with singlet substrates is prohibited. Catalyst (typically Ag) and harsh codnitions are thus required. Metalloenzymes achieve the same reactions in mild conditions using iron as a catalytic center, by reducing O_2 with 2 electrons to unleash its oxidizing power.[3] We explored this strategy of reductive O_2 activation using non-heme iron complexes, injecting electron via an electrode.[4] When the $Fe^{III/II}$ potential becomes low enough, the electrogenerated Fe^{II} complex $[L^2Fe^{II}]$ spontaneously reduces O_2 to superoxide at its $E(Fe^{III/II})$ reduction potential, a very accessible potential (>500 mV more favorable than the reduction of O_2 alone). While $L^2Fe^{III}(OTf)$ proved to be a good O_2 activator upon reduction but a poor oxidation system, its association with another complex $(TPEN)Fe^{II}(PF_6)_2$ generates a complementary tandem couple for electro-assisted oxidation of substrates, working at a very accessible potential: upon reduction, $L^2Fe^{III}(OTf)$ activates O_2 to superoxide and transfers it to $(TPEN)Fe^{II}(PF_6)_2$ leading *in fine* to the oxidation of thioanisole.[5]



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[4] N. Segaud, E. Anxolabehere-Mallart, K. Senechal-David, L. Acosta-Rueda, M. Robert, F. Banse, *Chem. Sci.* **2015**, *6*, 639-647.
[5] A. L. Robinson, J.-N. Rebilly, R. Guillot, C. Herrero, H. Maisonneuve, F. Banse, *Chem. Eur. J.* **2022**, *28*, e202200217.

CONFERENCIER

Pascal ANDREAZZA

Equilibrium and metastable behaviour of multi-metallic supported nanoparticles investigated by X-ray Scattering

P. Andreazza,[a] J. Pirart,[a] A. Lemoine,[a] H. Khelfane,[a] A. Coati,[b] Y. Garreau,[b] and C. Andreazza-Vignolle.[a]

[a] Université d'Orléans, CNRS, ICMN, 1b rue de la Férollerie, Orléans Cedex 2, France

[b] Synchrotron Soleil, L'Orme de Merisiers, Saint Aubin, Gif-sur-Yvette, France

pascal.andreazza@univ-orleans.fr

The growth of nanosized multimetallic alloys on a surface is a growing field of activity in the field of nano-objects. Among the methods, the technique of supported nanoalloy fabrication by condensation of metal atom vapors under ultra-high vacuum makes it possible to control the parameters of temperature and flow of atoms (and therefore of composition and size) in "ultra-clean" environmental conditions. However, these nano-objects are produced out of equilibrium, stabilized by the growth kinetics and/or by the presence of the substrate. They then change over time, with the temperature or their exposure to reactive gases. The morphologies (faceting of nanocrystals, wetting on a substrate), order states (atom arrangement: alloyed, segregated, ordered or disordered) or oxidation are in particular very dependent on the kind of atoms but also on the size of nanoalloys [2]. These "Nanoalloys" combine size reduction effects and multiple-element behaviors, which control their properties and functionalities. A coherent strategy is required to obtain from multi-scale investigations, the total description of nano-objects in terms of structure, morphology and organization, as well as in situ in growth or use conditions, than ex situ in an "post-mortem" state. The solution is to use methods, like X-ray total scattering [1] that probe local and average features, as well as in nanometer than in micrometer-sized scale, especially in situ and real time, combining small and wide-angle X-ray scattering techniques (SAXS and WAXS). SAXS measurements provide morphological features of nanoparticles (size, shape, phase separation, organization, coalescence…), while WAXS allows the determination of the structure at the atomic scale (crystalline, non-crystalline, alloyed, core-shell, janus…) [1-2], providing highly complementary data especially, with the support of electron microscopy (TEM) investigations [2,3]. Moreover, the quantitative structural analysis is highly facilitated and consolidated using atomistic simulations of nanoalloys using semi-empirical tight-binding potentials [2,5]. In addition, the x-ray beam grazing incidence (GISAXS-GIWAXS) highlights the near-surface contribution of deposited nanoalloys on substrate, while the anomalous variation of the scattering factor is able to disentangle complex chemical effect (core-shell transition, phase separation…) [3-5]. The development of the application of these WAXS and SAXS techniques to metallic nanoparticles and nanoalloys was facilitated by the access to high flux x-ray beams in synchrotron facilities, as well as by the development of analysis methodologies through dedicated softwares [4,5].

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Marie-Pierre GAIGEOT

Developments in algorithmic graph theory, supervised learning and game theory for theoretical chemistry

Sana Bougueroua,[a] Marie Bricage, [b] Dominique Barth,[b] Marie-Pierre Gaigeot[a]

Université Paris-Saclay, Univ Evry, CNRS, LAMBE UMR8587, Evry-Courcouronnes, France , Université Paris-Saclay, Univ Versailles Saint Quentin, DAVID, Versailles, France

mgaigeot@univ-evry.fr

In this presentation, we will present the theoretical developments that we have made with one PhD student and one Post-Doctoral researcher funded by LABEX CHARM$_3$AT for the coupling of molecular dynamics simulations with topological graphs and their associated algorithms, with game theory and supervised learning.

We will present the 2D-MolGraph molecular graphs[1] that we have developed in order to map the topology of any molecular system, we will show how these graphs are transferrable from isolated molecules to the condensed matter, for instance for complex inhomogeneous interfaces between solids and liquids.[2-3] With these graphs, one is able to automatically analyze and interpret the evolution with time of the conformations that are explored along molecular dynamics simulations, e.g. quantifying their changes and the types of molecular changes, quantifying the extent of collective H-Bonded network that can be formed in the liquid water at the interface with a solid, quantifying the distribution of sizes of H-Bonded polygons made by the water molecules, etc. Several applications will be briefly illustrated. The 2D-MolGraphs and the associated algorithms are distributed in the GaTewAY software.[4] Some recent applications in homogeneous catalysis can be found in ref. [5].

Going from a 2D topological graph to the associated 3D conformation of a molecule is another challenge that we have tackled by game theory and supervised learning methods. Our first attempts will be presented for peptides.[3]

Some references to our works:

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POST DOCTORANT

Augustin NOUAILLE

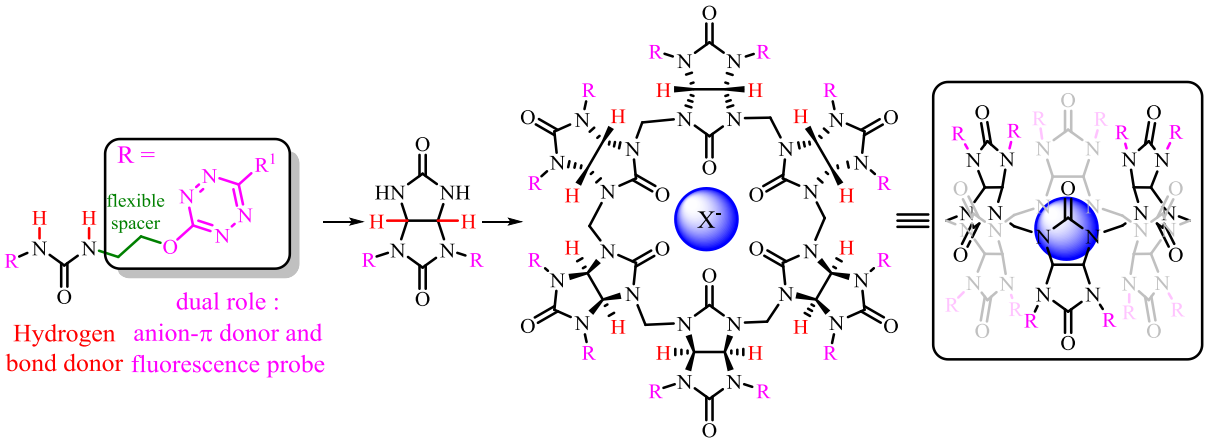
Synthesis and characterization of new anion receptors.

A. Nouaille,[a] **G. Pieters**[b], **D. Prim**[a], **M.-P. Heck**[b] **and A. Gaucher.**[a]

[a] Université Paris-Saclay, UVSQ, CNRS, Institut Lavoisier de Versailles, 78000, Versailles, France.
[b] CEA-Saclay, Service de Chimie Bioorganique et de Marquage, 91190, Saclay, France.

anne.gaucher@cea.fr / marie-pierre.heck@cea.fr

Anions are widely spread in several areas like biology, medicine, catalysis, or environment. For instance, chloride anion plays a key role in channelopathies such as the cystic fibrosis. Henceforth, the development of new anion receptors is a challenge in modern organic chemistry. The elaboration of such molecules is based on the formation of different non-covalent interactions (hydrogen bonds, anion-□ interactions, halogen bonds) and on the molecular recognition concept. Recently, new receptors were designed combining hydrogen bond donors and a s-tetrazine motive which play a dual-role of anion-□ donor and fluorescence probe.[1] Moreover, recent advance in the field of macromolecule as a cage to encapsulate anion has recently led to the development of bambusurils.[2] The aim of this project is to design a new family of anion receptors combining these two fields of research, and then to study their behaviour in the presence of anions (Cl^- and I^-) *via* NMR and fluorescence titration experiments.



[1] R. Plais, G. Gouarin, A. Gaucher, V. Haldys, A. Brosseau, G. Clavier, J. Salpin and D. Prim *ChemPhysChem* **2020**, 21, 1249.
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CONFERENCIER

Tsuyoshi KAWAI

Synergetic Approaches for Highly Sensitive Photoreactive Systems

Tsuyoshi KAWAI and Mihoko YAMADA,

[a] Graduate School of Science and Technology, Nara Institute of Science and Technology, NAIST, 8916-5 Takayama, Ikoma, Nara 30-0192, Japan

tkawai@ms.naist.jp

Among various organic photochromic molecules, those of based on hexatriene backbone such as diarylethene, DAE, and derivatives are most intensively studied. We have also studied some of related substances especially focusing on terarylene a sister substance of DAE. One of our targets has been to develop those of high sensitivity and we have successfully developed photon-quantitative reaction system, which indicates photochromic quantum yield close to unity. For conventional photoreaction systems, photochemical quantum yield does not exceed 100% and further exploration for higher sensitivity necessary to focus for enhancing molar-absorption coefficient and chain-like isomerization reaction which may derive photochemical quantum yield higher than unity. In this presentation, we will deliver our recent results for enhancing molar extinction coefficient of photochromic molecules and for chain like isomerization reaction systems with redox-induced ring-opening isomerization. We shall also discuss potential application for energy storage capability of our systems.

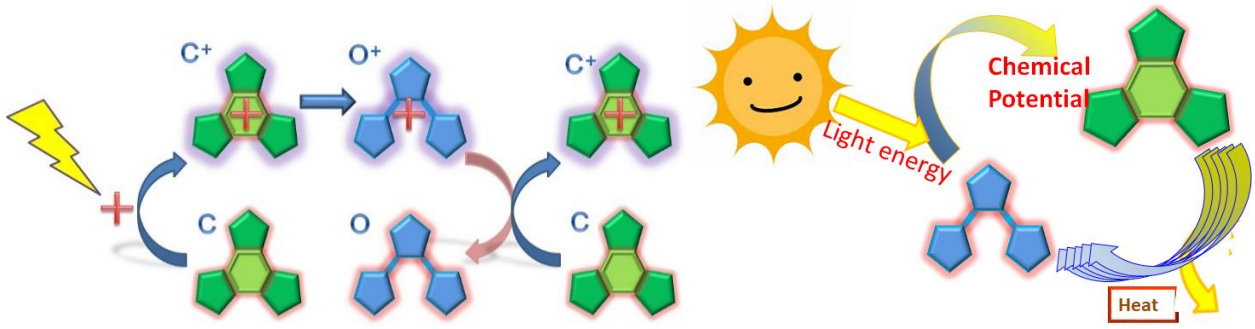

Figure 1 Possible energy cycle based on chain-ring-opening reactions of terarylenes

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Stéfania CACOVICH

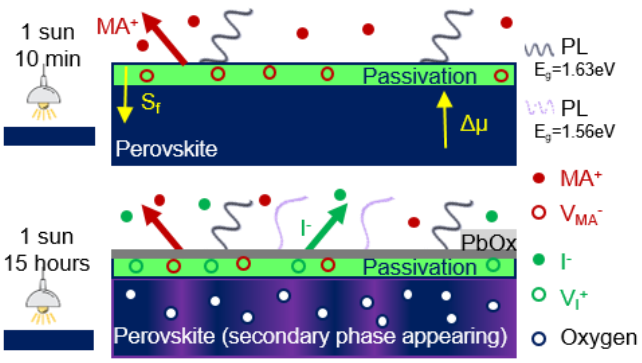
Multidimensional Photoluminescence Analysis for Photovoltaic Materials and Devices

[a] Institut Photovoltaïque d'Île de France (IPVF), CNRS, Ecole Polytechnique, IP Paris, Chimie Paristech, PSL, Palaiseau, 91120, France

stefania.cacovich@cnrs.fr

Photovoltaic (PV) devices offer a direct conversion of light source into electricity, providing a much-needed solution to meet climate targets and move towards a low-carbon economy. In the solar cell community there is a growing interest in the use and in the optimisation of optical imaging techniques, mainly based on luminescence analysis. Being contactless and non-destructive, they can be used at different steps of the life cycle of a solar cell, from the growth (in-situ) to the use (operando). Therefore, they constitute a powerful tool for characterizing charge transport mechanisms, allowing a direct access to the local photophysical properties of materials and devices.

During the past few years, hybrid perovskite solar cells have attracted a considerable amount of research and have undergone rapid development as next generation photovoltaics [1]. This emergent class of solar cells have become increasingly popular due to the opportunity of reaching high power conversion efficiency, while retaining a low manufacturing cost. In this talk, I will present how steady-state and time-resolved multidimensional photoluminescence imaging techniques can be used to probe the main optoelectronic and transport properties of perovskite thin films and full devices. A particular focus will be given to materials stability [2], and to new strategies envisaging the introduction of passivating agents based on organic cations at solar cells interfaces resulting in record efficiencies up to a value of 23.7%3 in p-i-n devices [3].



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[3] S. Cacovich et al. Imaging and Quantifying non-radiative Losses at 23% Efficient Inverted Perovskite Solar Cells Interfaces. *Nat. Comm.* **2022**, 13 (1), 1-9.

POST DOCTORANT

Julien ARI

Laser polarization-controlled crystallization and orientation of nonlinear optical nanocrystals in multicomponent glasses using a femtosecond laser for photonic applications

J. Ari[a], M. Cavillon[a], M. Lancry[a], O. Plantevin[b], L. Houel-Renault[c], and B. Poumellec[a]

[a]Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), Université Paris-Saclay, CNRS, 91405 Orsay, France

[b]Laboratoire de Physique des Solides (LPS), Université Paris-Saclay, CNRS, 91405, Orsay, France

[c]Institut des Sciences Moléculaires d'Orsay (ISMO), Université Paris-Saclay, CNRS, 91405 Orsay, France

julien.ari@universite-paris-saclay.fr

Femtosecond (fs) laser direct writing (FLDW) is a powerful and versatile tool to fabricate a large variety of components inside amorphous materials such as glasses (e.g. Bragg gratings, waveguides, graded index lenses, birefringent optics). By controlling the fs-laser parameters it becomes possible to generate stable and oriented nanostrutures inside the glass. As an example to this approach, $LiNbO_3$ nanocrystals, having properties such as piezo-electricity and ferro-electricity, can be photo-crystallized in Li_2O-Nb_2O_5-SiO_2 (LNS) glasses, and recently extended to Li_2O-Nb_2O_5-SiO_2-B_2O_3 (LNSB) glass system [1]. A unique feature of this light/matter interaction is the possibility to control the polar axis orientation of the $LiNbO_3$ nanocrystals by tuning the light polarization during the irradiation of the glass material [2].

The objective of this LabEx project is to investigate the embedding and elemental distribution of rare earth (RE) Eu^{3+} ions inside the nanocrystals induced by fs-laser irradiation of LNSB doped glasses. The potential incorporation of RE ions into these $LiNbO_3$ nanocrystals will contribute to develop new kind of integrated optic materials (laser sources, miniaturized sensors or high density optical storage) that will combine both non-linear optics with RE spectroscopic properties. The investigation of fs-laser induced crystallization in Eu^{3+}-doped LNSB glasses will be presented with the characterization of luminescence properties in the crystallized areas [3].

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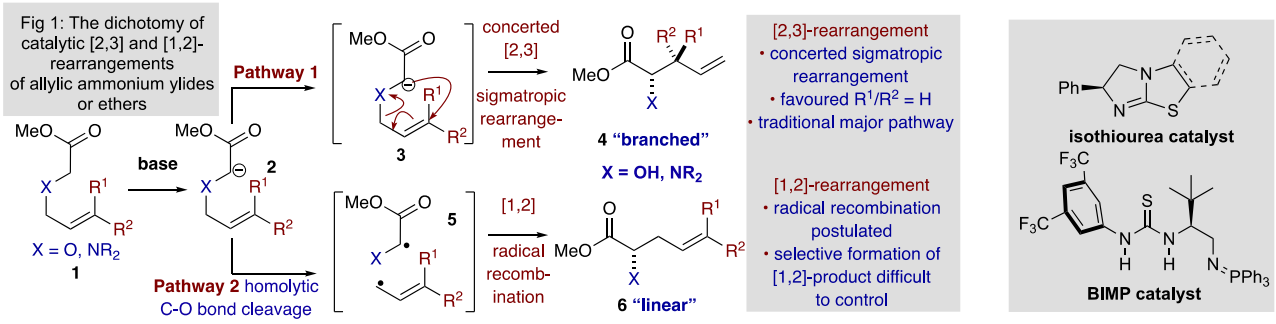
Andrew D. SMITH

Catalytic Enantioselective [2,3]- and [1,2]-rearrangements of allylic ammonium ylides and ethers

[a] EaStCHEM, School of Chemistry, University of St Andrews, St Andrews, Fife, Scotland, UK. KY10 3TH

ads10@st-andrews.ac.uk

Stereoselective [2,3]-sigmatropic rearrangements have great utility in organic synthesis.[1] In particular, their ability to form carbon-carbon bonds with high diastereo- and enantiocontrol through well-defined and predictable transition states under mild reaction conditions makes these processes attractive for the synthesis of complex targets. In this context, the [2,3]-sigmatropic rearrangement of allylic ethers or allylic ammonium ylides **1** allows the preparation of bespoke □-functionalised stereodefined "branched" alcohol or amine derivatives **4** (Fig 1, Pathway 1). This process is well described in the literature with a concerted pathway via **3** predicted through orbital symmetry constraints. However, an alternative reaction pathway, that of the corresponding [1,2]- rearrangement, leads to the alternative "linear" product. As a concerted mechanism for a [1,2]-rearrangement is thermally-disallowed based on orbital symmetry, the mechanism is proposed to proceed through initial deprotonation, followed by homolytic *C–O* bond cleavage to generate a diradical pair **5**, which undergoes radical-radical recombination to form the new bond and generate **6** (Pathway 2).[2] This di-radical pathway has been contentiously debated for decades; subtle changes in electronic and steric structure of the substrate is known to bias either the [1,2]- or [2,3]-rearrangement pathway, often leading to uncontrolled formation of both products. Irrespective of the mechanistic pathway there is extremely limited precedent (no examples to date) to promote the catalytic enantioselective [1,2]-rearrangements of allylic ammonium ylides and ethers. This talk will demonstrate the generation of methodology for the selective promotion of catalytic enantioselective [2,3]- and [1,2]-variants of these processes using isothioureas and BIMP organocatalysts, as well as mechanistic studies of these reactions.



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Aurélien DE LA TORRE

Copper Catalysis-Enabled Enantioselective Cycloadditions

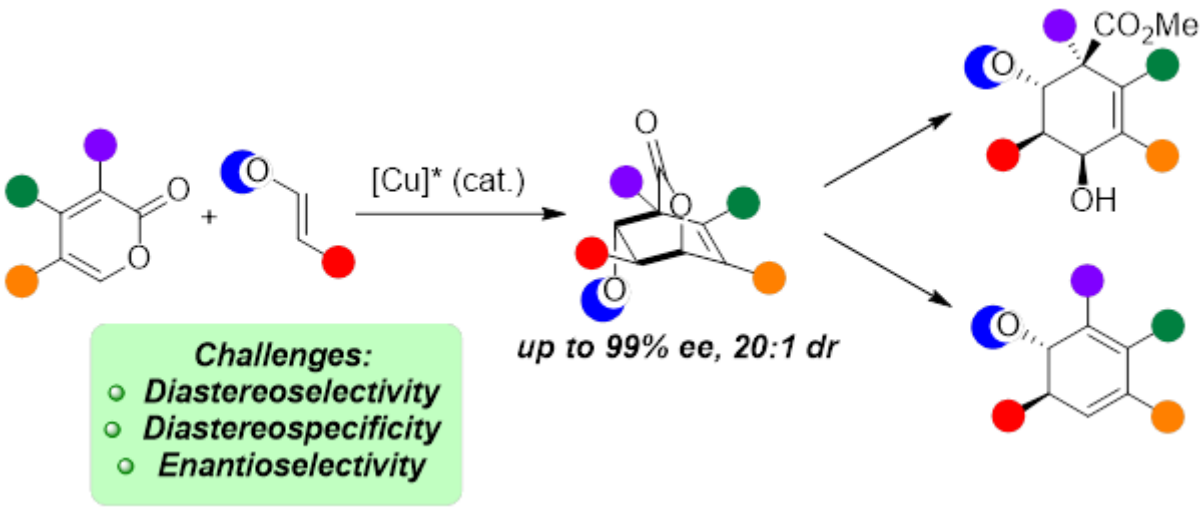
G. Huang,[a] Cyrille Kouklovsky, B. Maryasin and A. de la Torre.[b]

[a] Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182 CNRS Université Paris-Saclay, 19 Avenue des Sciences, 91400 Orsay

aurelien.de-la-torre@universite-paris-saclay.fr

The inverse electron demand Diels-Alder (IEDDA) cycloaddition of electron-deficient 2-pyrones with electron-enriched dienophiles is a powerful synthetic method, which was often employed in total synthesis in the last decades.[1] Nevertheless, most of these applications were limited to racemic syntheses, as examples of enantioselective versions of this reaction are scarce.

In this work, we develop an enantio- and diastereoselective IEDDA reaction of 2-pyrones with substituted acyclic enol ethers (Scheme 1).[2] The resulting bicyclic lactones are obtained in high yield and high ee, and can be converted to complex enantio- and diastereo-enriched cyclohexadienes and cyclohexenes. In particular, the use of acyclic enol ethers allows us to investigate mechanistic aspects of the reaction.



Scheme 1 : Enantioselective IEDDA reactions between 2-pyrones and acyclic enol ethers

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POST DOCTORANT

Eric DAIANN SOSA CORRIZO

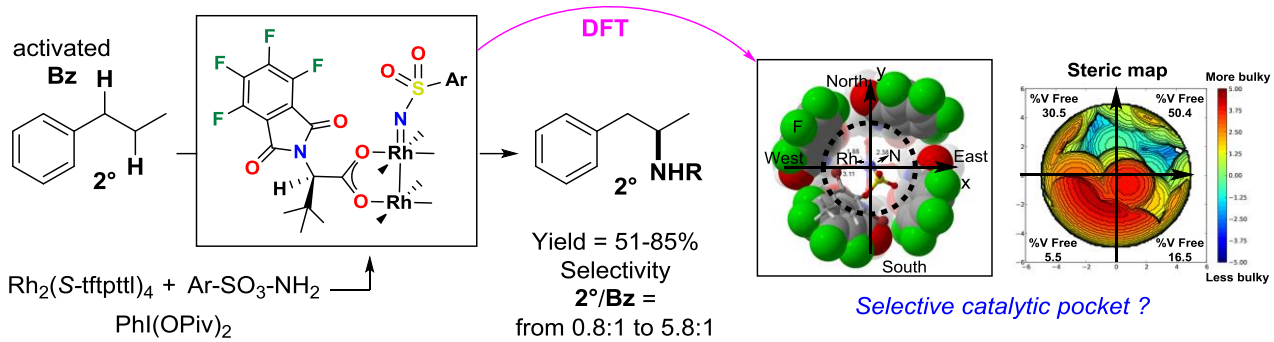
Switching the selectivity in the Rh(II) Catalyzed C(sp^3)-H amination of propylbenzene: insights from a DFT viewpoint

E. Daiann Sosa Carrizo,[a,b] Erwan Brunard,[a] Tanguy Saget,[a] Marie Sircoglou,[b] and Philippe Dauban.[b]

[a] Université Paris-Saclay, Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette, France
[b] Université Paris-Saclay, Institut de Chimie Moléculaire d'Orsay, CNRS, 91405, Orsay, France

daiann.sosa-carrizo@universite-paris-saclay.fr

The design of site-selective C−H functionalization reactions is a great challenge with important applications in organic synthesis. Dirhodium(II) complexes are among the best catalysts to perform selective insertion of nitrenes into C(sp^3)-H bonds.[1] In this respect, recent experimental results showed a remarkable selectivity for the amination of propylbenzene with the Rh_2(*S*-tfpttl)$_4$ complex as catalysts.[2] To understand this selectivity, we perform DFT calculation to reveal the factors guiding the catalytic system. Our strategy involves evaluating the mechanism to disclose the electronic or steric factors controlling the selectivity between the secondary (2°) vs benzylic (Bz) C−H bond.



In this study, we computed the general mechanism for the functionalization of the C-H bond, which involves either i) a concerted C–H insertion or ii) a stepwise process of hydrogen atom abstraction, followed by radical recombination. The mechanism found computationally indicates that the concerted singlet mechanism was favoured, preferentially occurring at the non-activated 2° position as observed experimentally. We also applied the Steric map plot tool to understand the interaction between the catalyst and substrate controlling the selectivity. Our results evidenced the role of the catalysts' pocket in stabilizing key intermediates, and the influence the activations barriers for the C–H amination.

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CONFERENCIERE

Myrtil KAHN

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

M. L. Kahn

Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse cedex 04, France

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 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. The multi-solublility of these ZnO NPs was achieved using amino-PEG ligands.[2] New hybrid materials,[3] as well as liquid crystal ligands for controlled growth of ZnO NPs were also developed.[4] The importance of the correlation between width and length in the shape analysis of anisotropic nanoparticles was demonstrated using a 2D size plot.[5]. Full characterization by NMR spectroscopy of the surface of such ZnO NPs demonstrates that the surface is rather complex,[6] and can exhibit surprising ferroelectric properties.[7] Preparation of other metal oxides (□-Fe_2O_3, FeO, CoO, $CoFe_2O_4$, CuO, SnO_2) has also been carried out and these materials have been studied for the development of devices such as nanovaristors,[8] UV detector,[9] Radiosensitizing and MRI contrast agent,[10] and gas sensors,[11] Recently, we have developed a secured nanosynthesis–deposition aerosol process for composite thin films incorporating highly dispersed nanoparticles.[12] Such approach is now being considered for the design of thin films of interest for, for example, H_2 production and secure H_2 storage.[13]

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Laurie CALVET

Integrating smart sensors and materials into bio-inspried hardware

L. E. Calvet

Centre de Nanosciences et Nanotechnologies, 10 boulevard Thomas Gobert, 91120 Palaiseau

laurie.calvet@c2n.upsaclay.fr

Increases in computing performance have led to significant advances in computing systems, ranging from handheld devices to supercomputers, and have enabled rapid advances in Artificial Intelligence (AI). This progress is closely linked to the continued shrinking of the complementary metal-oxide-semiconductor (CMOS) technology feature size, which has now reached fundamental barriers. To improve capabilities of future AI systems, researchers are exploring new computational paradigms, which can exploit the specific needs of a set of applications and the interactions between hardware, software and algorithms in a computing system. We can distinguish two large classes of bio-inspired hardware implementations. The first focuses on using lower energy consuming artificial neuro-architectures for reducing the power consumption of large computing centers, which continually perform calculations. The second considers new portable systems, whose neuro-inspired design principles enable smart functionalities that are not possible with more traditional implementations. The input for such portable systems can be based on smart responsive materials, such as those explored in the LabEx CHARMMMAT. In this talk, I will give an overview of some of the novel computing paradigms employed in my research that incorporate novel materials and sensors.

After introducing some basic notions of bio-inspired computing, I will show how spiking electronic neurons can be used to convert sensor data into features that can then be used for classification tasks [1]. This conversion can result in a significant energy reduction for eventual devices, enabling very low power operation. I will then discuss how such spiking neurons can be integrated into low cost and low energy consuming organic electronics and how such materials might more easily integrate with some of the smart materials and interfaces of interest to the CHARMMLAT community. In the last part of my talk will I introduce optically spiking neurons [2] and discuss how photochromic materials can be used to create a fully optical neuro-inspired architecture of classification.

This research is supported by ANR contract BAYOEN, ANR-21-FAI1-0006-01, the Nanosaclay LABEX project CANAPO, the ANR contract PHOTOMIC.

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POST DOCTORANTE

Julie PHAM

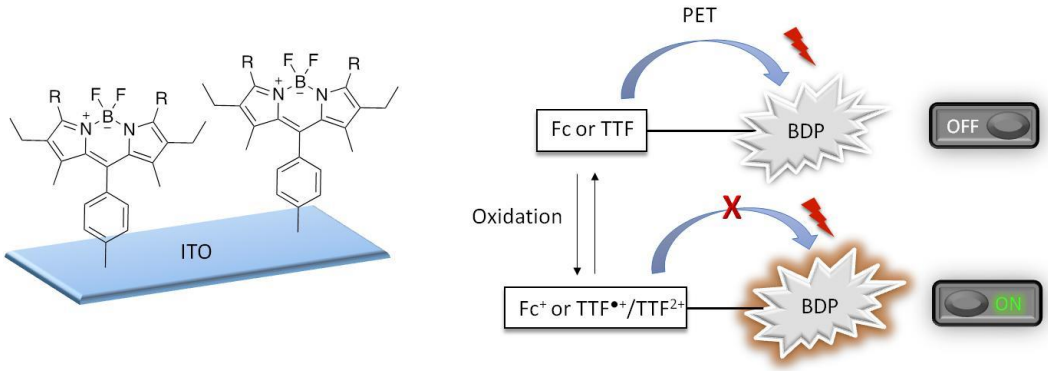
Electrofluorochromism of surface-confined BODIPYs.

J. Pham,[a,b] J. Audibert,[a] J. Rabah,[b] M-H Ha Thi,[c] E. Allard,[b] F.Miomandre[a]

[a] PPSM, Ecole Normale Supérieure Paris Saclay, Gif-sur-Yvette, France
[b] ILV, Université Versailles St-Quentin, Versailles, France
[c] ISMO, Université Paris Saclay, Orsay, France

julie.pham@ens-paris-saclay.fr

Boron dipyrromethene (BODIPY) chromophores exhibit fluorescence which can be quenched by photo-induced electron transfer (PET) when coupled to strong electron donors such as tetrathiafulvalene (TTF) or ferrocene (Fc).[1-3] The extent of donor contribution is strongly dependent on the linker nature and position in the dipyrromethene ring. The reversible redox behaviour of TTF and Fc allows for modulation of the fluorescence as a function of oxidation state. We compared the emission profiles of BODIPY-donor dyads under chemical and electrochemical oxidation of the donor TTF and Fc in the α- or β- position. BODIPY dyads displaying a modulation of fluorescence as a result of donor oxidation/reduction in solution were derivatized for attachment to a surface of indium tin oxide (ITO) and the fluorescence modulation of the self-assembled monolayer was assessed.



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CONFERENCIERE

Alessandra QUADRELLI

ALD Growth of ultrathin films and mechanistic insight by surface organometallic chemistry

Elsje Alessandra Quadrelli

IRCELYON, Univ de Lyon, UMR 5256–CNRS–Univ. Lyon 1 , Villeruabnne -France

elsje.quadrelli@catalyse.cnrs.fr

Surface organometallic chemistry (SOMC), developed since the 1970's,[1] and still vigorously present in the literature, [1b] is a surface modification technique of (mostly) oxide supports with organometallic precursors. Its strongest conceptual basis is molecular inorganic and organometallic chemistry, its originality is to apply it to solids, its biggest successes have been until now heterogeneous catalysts often based on isolated metal atoms.

We have extended this approach into the field Atomic Layer Deposition (ALD), a thin-film growth technique with major applications in fields such as microelectronics and energy converting devices. We are showing that this original approach is particularly valuable to yield exquisitely well-defined thin films with control down to the monolayer, otherwise difficult to reach. A major milestone was the first growth of an atomically thin MoS_2 layer on silicon wafers by ALD.[2a] We have since extended it to titania nanotubes,[2b,c] followed the growth of WS_2 [3] and TiS_2[4] layer by layer, protected $BiVO_4$ photoanaodes with alumina,[5] and grew a ZIF-8 MOF layer[6] as functioning methanol sensor (see fig 1). Some of these examples will be shown herein.

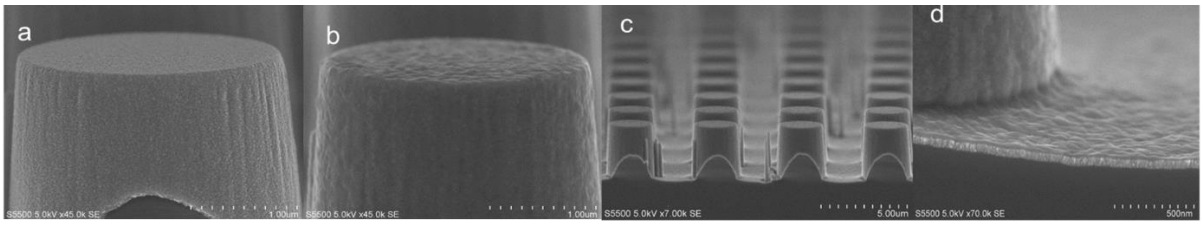

Figure 1. Scanning Electron Micrographs of (a) starting ZnO-covered silicon micropillars ; (b) (c) (d) ZIF-8 covered micropillars obtained through the gas-phase cycling process described herein.

***Acknowledgements*:** *All the co-authors and funding agencies of works [2-6] are kindly acknowledged.*

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Clémence SICARD

Mesoporous Metal-Organic Frameworks for the encapsulation of Microperoxidase-8 and other bio-entities.

E. Gkaniatsou,[a] X. Kesse,b A. Permyakova,[a] R. Ricoux,b J.P. Mahy,[b] N. Steunou,[a] C. Sicard, [a]

[a] Institut Lavoisier de Versailles, UVSQ, CNRS UMR 8180, Univ. Paris-Saclay, Versailles, Fr.

[b] LCBB, ICMMO, UMR 8182, Université Paris Sud, Université Paris-Saclay, Orsay, Fr

clemence.sicard@uvsq.fr

The combination of Metal-Organic Frameworks (MOFs) with biological entities (enzymes, viruses,...) has recently arise as an alternative and promising strategy to answer the limitations of traditional immobilization matrices, resulting in the design of novel functional biomaterials with promising properties.[1] We will present the use of MIL-101(Cr) nanoparticles as an immobilization matrix for the micro-enzyme microperoxidase-8 (MP-8).[2] MP-8 encapsulation in the mesoporous cages of MIL101(Cr) was a valuable strategy to enhance its catalytic activity under acidic or oxidative conditions and to maintain long-term, recyclable catalytic activity. The role of the MOF to enhance selectively the bio-degradation of organic dyes will also be demonstrated (Fig. 1). The impact of MIL-101 functionalization on the immobilization efficiency as well as on the bio-catalytic activity will be also discussed. [3] The last part of this presentation will focus on our efforts for MOFs synthesis in presence of biological entities under compatible conditions with the preservation of the biological function. We will concentrate on the synthesis and characterization of MOFs-based living materials.[4]

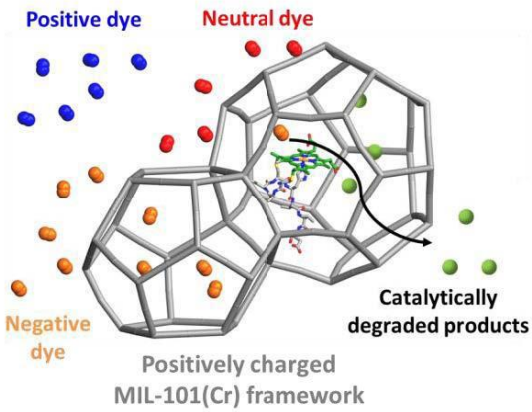

Figure 1. Schematic representation of MP-8 encapsulation within MIL-101(Cr) promoting substrate selectivity.

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CONFERENCIER

Alain BRUNELLE

Fine and complex organic-inorganic layers in old paintings revealed by TOF-SIMS mass spectrometry imaging

A. Brunelle[a]

[a] Sorbonne Université, CNRS, Laboratoire d'Archéologie Moléculaire et Structurale, LAMS, 4 place Jussieu, 75005 Paris, France

Alain.Brunelle@cnrs.fr

When painting, an artist works with diverse mixtures of pigments and binders, layered in expert gestures to achieve the intended rendering. The mastery of the binder properties allows them to exploit their possible optical effects. The layers can be down to a few micrometers thick. Understanding the internal structure of a painting is important to better understand and preserve it. Ancient paintings are several centuries old, during which the various heterogeneous mixture of inorganic and organic compounds have interacted with each other and their environment. Sub-millimeter scale cross-sections of the painting, removed with a blade, offer simultaneous access to all the layers. To analyze such an object comes with constraints. They are fragile, unique and should be kept as intact as possible to allow subsequent examinations with other techniques.

TOF-SIMS mass spectrometry imaging can give the localization and identification of both pigments and organic materials, bringing out indications relating to their nature, origin, or state of preservation [1,2], and at a sub-micrometer scale. The instrument used can reach a lateral resolution down to 400 nm while preserving a mass resolution of several thousands, thanks to the delayed extraction of the secondary ions. TOF-SIMS imaging is a surface-sensitive analytical method requiring the sample surface to be flat and clean, so the preparation step is crucial. The identification of binders can still be ambiguous, since organic materials detected can also be degradation products or surface contaminants. Moreover, the yield of secondary ions varies according to the layer nature and local environment. A local tuning of the analysis parameters on small-analyzed areas and a knowledge of the expected characteristic ions for each type of binder, proved to be of further importance to avoid erroneous conclusions [2,3]. The motivations of these analytical improvements will be exemplified with the results obtained from the analysis of the chemical composition of fine layers cross-sections from an ancient painting analyzed this way, the *Infant Bacchanals* (Nicolas Poussin, 1626, Museo Nazionale d'Arte Antica, Rome). With the support of the expertise of art historians, this allows a better insight into the artwork's stories. In this case it has been shown that a fine surface layer was changing the final aspect of the painting, making it looks like a tempera painting, while being in fact an oil painting below.

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Rachel MEALLET

Luminescent Organic Nanoparticles as tools for biological or health issues.

Gilles Clavier,[b] Yasukuni Ryohei ,[c] Pan Miaobo,[a] Taufik Indra Rukmana,[a] Gabriela Moran-Cruz,[a] Jean-Baptiste Bodin,[a] Nicolas Tsapis [d], Yoichiroh Hosokawa,[c], Rachel Méallet[a]

[a] Institut des Sciences Moléculaires d'Orsay, UMR 8214, Fac. Sciences, Univ. Paris-Saclay, Orsay

[b] Laboratoire de Photophysique et Photochimie Supra-et Macro-moléculaires, UMR 8531, ENS-Paris-Saclay, Gif sur Yvette

[c] Nara Institute of Science and Technology, BioProcess Engineering, Nara, Japan

[d] Institut Galien Paris-Saclay, UMR 8612, Fac. Pharmacy, Univ. Paris-Saclay, Châtenay

rachel.meallet-renault@universite-paris-saclay.fr

For few years we have been developing organic fluorescent nanoparticles (FNPs) thanks a controlled polymerization in micro-emulsion. The FNPs are flexible, tunable and versatile: emission brightness, colors(s), size and surface chemistry can easily be controlled through the choice, combination, and organization of their building blocks.

We have developed water-soluble core-shell boron-dipyrromethene (BODIPY) polymeric particles [1] with different surface functional groups [2]. Core contains BODIPY, which depending on its substitute group, could emit green or red spectrum. Shell consists of hydrophylic block copolymers such as PAA-PEO.

We will show how such red-FNPs can be used to detect bacteria growth on a surface, thanks to pH sensitivity [3].

In a second part we will discuss how green-FNPs could be used to study inter- and intra-diffusion in cell plants [4].

Finally we will introduce newly developed nanovectors for photoacoustic imaging [5].

[1] *J. Phys. Chem. C.* **2014**,118, 13945, 10.1021/jp502790w

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[4] *Applied Physics Express* **2020**, 13, 117002, 10.35848/1882-0786/abc490

[5] *ACS Appl. Mater. Interfaces* ***2022***, 40501, 10.1021/acsami.2c04874

POST DOCTORANT

Parisa BAYAT

Comprehensive structural assignment of glycosaminoglycans by aerolysin nanopore

Parisa Bayat,[a] Charlotte Rambaud,[a] Bernard Priem,[b] Matthieu Bourderioux,[a] Mélanie Bilong,[a] Salomé Poyer,[a] Manuela Pastoriza-Gallego,[c] Abdelghani Oukhaled,[c] Jérôme Mathé,[a] Régis Daniel[a]

[a] Université Paris-Saclay, Univ Evry, CNRS, LAMBE, 91025, Evry-Courcouronnes, France
[b] CNRS, CERMAV, University Grenoble Alpes, 38000 Grenoble, France
[c] CY Cergy Paris Université, CNRS, LAMBE, 95000 Cergy-Pontoise, France

parisa.bayat@univ-evry.fr

Sequencing of polysaccharides is lagging behind compared to the very advanced situation of the sequencing of the two other major families of bio-polymers, nucleic acids and proteins, for which effective methods of structural analysis have been available for decades. The need for such methods is particularly felt for bioactive polysaccharides and among them glycosaminoglycans (GAGs).

GAGs are highly sulfated linear polysaccharides expressed at the cell surface and in the extracellular matrix where they play a dominant role in the communication of cells with their environment [1]. Comprising of disaccharide units, GAGs present an extraordinary structural complexity due to their non-template driven biosynthesis that results in their chemical heterogeneity and a broad diversification of structure.

Faced with this situation, a powerful solution is provided by the single-molecule detection and characterization based on the translocation through nanopores. This technique has been applied to GAGs by exploiting the confinement properties of the aerolysin nanopore. Heparin, chondroitin sulfate, dermatan sulfate, heparosan and hyaluronic acid saccharides were analyzed and distinguished, showing that aerolysin nanopore can detect and characterize GAGs with various sulfate patterns, osidic bonds and epimers of uronic acid residues. Afterwards, this ability of the aerolysin nanopore to probe all these structural determinants of GAGs has been exploited to follow the regioselective desulfation of heparin by a sulfatase enzyme [2].

The results of the study show for the first time the detection and resolution of different sequences of GAGs according to the different modifications distributed along the chains. The discrimination of the building blocks of GAGs is an essential step towards a sequencing pathway for these polysaccharides.

[1] A. J. Lepedda, G. Nieddu, M. Formato, M. B. Baker, J. Fernández-Pérez, Lorenzo Moroni, *Front. Chem.*, **2021**, *9*, 680836.

[2] P. Bayat, C. Rambaud, B. Priem, M. Bourderioux, M. Bilong, S. Poyer, M. Pastoriza-Gallego, A. Oukhaled, J. Mathé, R. Daniel, *Nat. Commun.* **2022**, *13*, 5113.

POSTERS

INTERVENANTS	LABORATOIRE	TITRE DU POSTER
Abdul Halim OBEID	Université Paris Saclay ICMMO - ECM	Iron-catalyzed carbon-carbon double bond isomerization
Guillaume FORCE	Service de Chimie Bio-organique et de Marquage, DRF-JOLIOT-SCBM, CEA	CyClick: A Click Approach for Copper-Catalyzed Construction of Drug-like Macrocyles
Mihoko YAMADA	Graduate School of Science and Technology, Nara Institute of Science and Technology	Photochromic Tetrathienyl Corannulene Compound with High Photosensitivity
Rajesh BISHT	ENS Paris-Saclay, CNRS, PPSM	Naphthopyran doped mechanochromic polymers for mechanical strain/stress sensors
Robert B. PANSU	Université Paris-Saclay, CNRS, ENS Paris-Saclay, CentraleSupélec, LuMIn, Inst. d'Alembert	De l'analyse des déclins de luminescence en phase solide
Yutzil SEGURA	Institut de Chimie Physique, CNRS, Université Paris-Saclay,	Copper-based Nanoparticles for CO_2 Electroreduction
Baptiste AMOUROUX	ENS Paris-Saclay, CNRS, PPSM	Towards glyphosate optical sensor

Iron-catalyzed carbon-carbon double bond isomerization

Abdul Halim OBEID, Richard GIL, Sophie BEZZENINE, and Jérôme HANNEDOUCHE

Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), Equipe de Catalyse Moléculaire, Université Paris-Saclay, 91400 Orsay, France

abdul-halim.obeid@universite-paris-saclay.fr

Carbon-carbon double bond is one of the most important and versatile functionalities in organic chemistry. Among the plethora of synthetic methods available to introduce this functionality, Metal-catalyzed isomerization giving rise to a new isomer has become a fundamental and strategic synthesis tool with extensive applications in the production of high value molecules as it offers a waste-free process with 100% atom efficiency and no need for stoichiometric exogenous reagents.[1] This reaction has been widely investigated using noble metals-based catalysts such as rhodium, palladium, or iridium which are rare, expensive, and relatively toxic.[2] Thus, the development of alternative catalytic isomerization processes remains a major challenge in modern metal catalysis. Iron catalysis has emerged as a cost effective and an eco-friendly alternative for sustainable development.[3] Although many isomerization methodologies using abundant metals mainly cobalt-based catalysts have been reported, iron-catalyzed isomerization is still underdeveloped and often integrated into tandem isomerization-functionalization processes that drive the isomerization step.[4]

Thanks to our expertise in earth abundant metal-based catalysis,[5] herein we present our contributions to disclose a challenging iron-catalyzed carbon-carbon double bond isomerization methodology using a low-coordinate iron alkyl complex. This work is combined with mechanistic studies for an elucidation of the catalytic system involved in this process

[1] J. J. Molloy, T. Morack and R. Gilmour, *Angew. Chem. Int. Ed*. **2019**, *58*, 2.
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[5] a) E. Bernoud, P. Oulié, R. Guillot, M. Mellah and J. Hannedouche, *Angew. Chem. Int. Ed*. **2014**, *53*, 1; b) C. Lepori, E. Bernoud, R. Guillot, S. Tobisch and J. Hannedouche, *Chem. Eur*. J. **2019**, *25*, 835; c) C. Lepori, R. Guillot and J. Hannedouche, *Adv. Synth. Catal*. **2019**, *316*, 714.

CyClick: A Click Approach for Copper-Catalyzed Construction of Drug-like Macrocyles

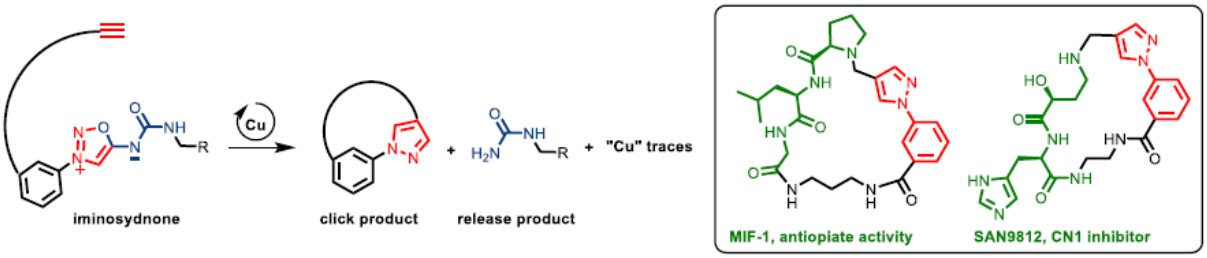
G. Force,[a] F. Taran[a] and E. Schulz[b]

[a] Service de Chimie Bio-organique et de Marquage, DRF-JOLIOT-SCBM, CEA, Université Paris-Saclay, 91191 Gif-sur-Yvette (France)

[b] Institut de Chimie Moléculaire et des Matériaux d'Orsay, Equipe de Catalyse Moléculaire, UMR 8182, Université Paris-Saclay, 91405 Orsay (France)

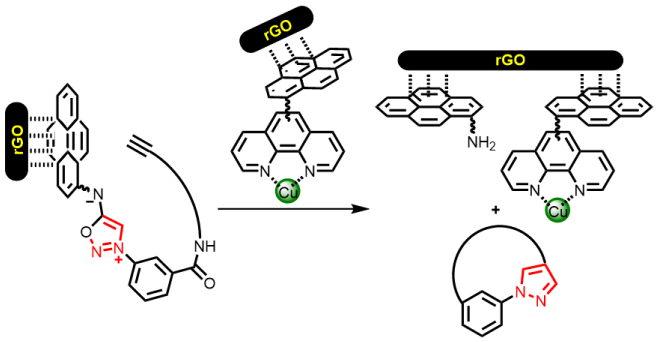
guillaume.force@cea.fr, frederic.taran@cea.fr

Cyclic drugs, in particular cyclic peptides and pseudo-peptides have recently received considerable attention in the pharmaceutical industry. Their structural preorganization compared to their linear counterparts provide them with high biostability, cell permeability and enhanced potency.[1] However, despite their importance, the synthesis of cyclic compounds remains challenging, with the difficile preparation of linear precursor and tedious purifications. Our laboratory have been working on the discovery of new biorthogonal tools and developed a click and release reaction of iminosydnones with cycloalkynes for protein modification, drug release and target-fishing applications.[2] Based on the recent developments of a new "click and release" reaction using a copper catalyst and aza-iminosydnones,[3] we decided to investigate the intramolecular macrocyclization of peptides using iminodydnones (Scheme 1).



***Scheme 1**: Cu-catalyzed click & release reaction leading to targeted macrocyclised compounds*

Preliminary results show limitations such as challenging purifications of the click and release products and the presence of copper traces associated with the cyclic product. One approach to overcome these problems is to develop a click type, Cu-catalyzed intramolecular cyclisation as a key step and the use of non-covalent immobilization (π-stacking) of pyrene-tagged catalysts and reactant on carbon supports like rGO (reduced Graphene Oxide) for easy removal and recovery (Scheme 2).[4]



***Scheme 2**: Supported intramolecular Cu-catalyzed click&release*

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[4] D. Didier *et al. Tet. Asymmetry* **2013**, *24*, 769.

Photochromic Tetrathienyl Corannulene Compound with High Photosensitivity

M. Yamada, T. Sawazaki, M. Fujita, F. Asanoma, Y. Nishikawa, and T. Kawai.

Graduate School of Science and Technology, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

myamada@ms.naist.jp

Terarylene derivatives show photochromism through 6π-photocyclization and cycloreversion. They offer additional structural flexibility at the central bridging unit in comparison with diarylethene. 20π electron curved aromatic compound, corannulene, shows photophysical properties different from the typical planar aromatic compounds, which are derived from the geometrically and electronically non-equivalent concave and convex surfaces and their bowl-to-bowl inversion behavior. In this work, we synthesized new photochromic compounds with two units of terarylenes fused by a curved aromatic corannulene and studied their photochromic behavior by comparing with terarylene derivatives with a planar aromatic skeleton.

We designed photochromic tetrathienyl corannulene compounds, **1** and **2**, by fusing two units of photochromic terarylene with a curved aromatic corannulene. Their absorption spectra changed by UV-irradiation and returned to the original state by following vis-irradiation, which indicated the photochromism of **1** and **2**. In this photocyclization, **1** showed high photosensitivity with a large molar absorption coefficient of 8.2×10^4 M^{-1} cm^{-1} and practically photon-quantitative photocyclization. On the other hand, a reference compound with a terarylene unit and a planar aromatic phenanthrene **3** showed no photochromic behavior. High sensitivity of **1** was rationalized by energy migration, the predominance of the photoreactive atropisomers, and the shortened distance between reactive carbons induced by the curved structure.

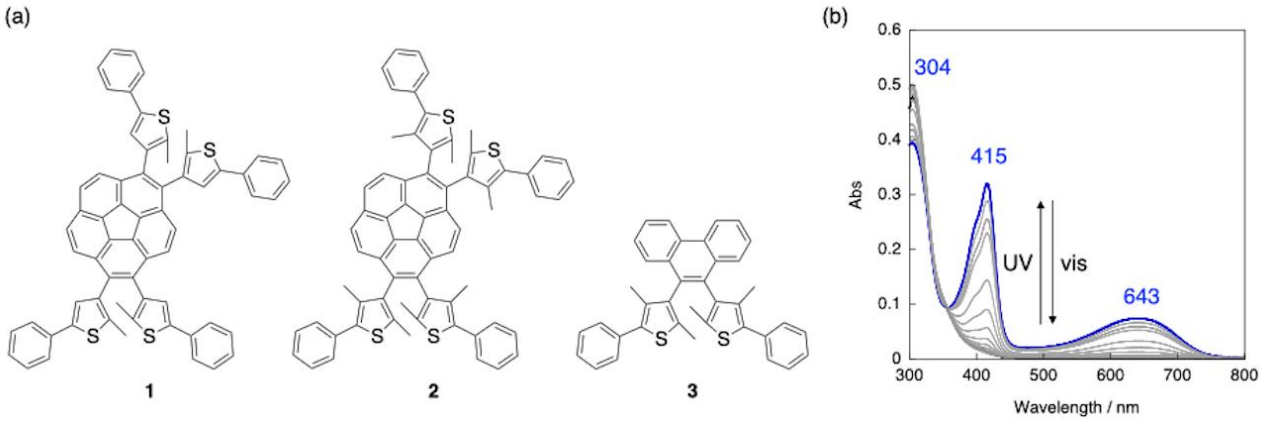

Figure 1. (a) The molecular structures of **1**, **2**, and **3**, and (b) the absorption spectral change of **1** in toluene under photoirradiation.

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Naphthopyran doped mechanochromic polymers for mechanical strain/stress sensors

R. Bisht,[a] B. Poggi [a] and C. Allain.[a]

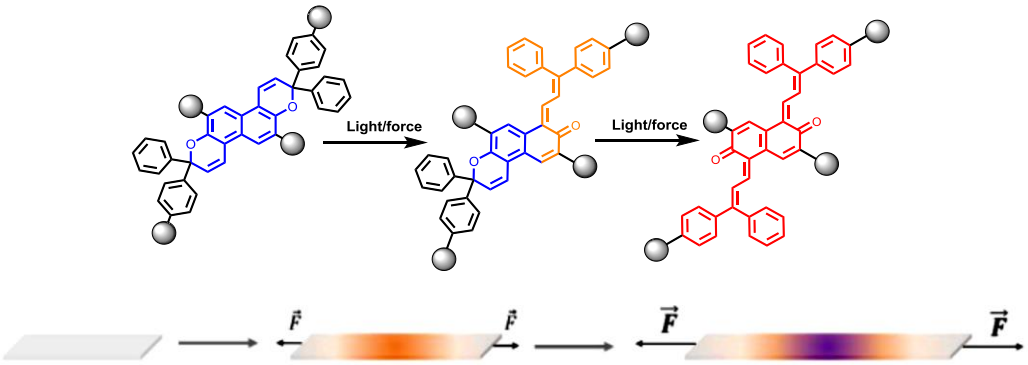
[a] ENS Paris-Saclay, CNRS, PPSM, 91190 Gif-sur-Yvette,

rajesh.bisht@ens-paris-saclay.fr

The detection of mechanical stresses is a major challenge to controlling the evolution of the mechanical properties of a material and detecting fractures or deformations. This would be particularly useful in the fields of transport, construction, security, and packaging. [1]

Organic mechanophores are molecules that change their absorption and/or emission spectra upon being subjected to mechanical stress. Covalent incorporation of these mechanophores into polymer matrices can result in useful polymeric materials sensitive to stress/strain. Isomerization-based photochromes such as naphthopyran (NP) are one of the common types of molecules that can also act as mechanochromophores.[2–4]

In this report, we designed and synthesized bis-naphtopyran-based novel photochromes which consist of two napthopyran units conjoined with the same core. These molecules consist of a spiro-junction that undergoes ring-opening under external force, resulting in resonance structures causing a color change. These molecules can exhibit multi-stage photochromism response under UV and visible light due to the presence of two photochromic units in conjugation. The study of bond-breaking mechanisms and the incorporation of these mechanochromophores into a range of polymer matrices for stress/strain sensing is also carried out.



Scheme 1. *Expected transformation of the target molecules upon exposure to light/force to give multi-chromic mechanophore*

[1] Stuart et al, *Nature Mater* **2010**, *9*, 101–113.

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De l'analyse des déclins de luminescence en phase solide

Robert Bernard Pansu[a]

[a] Université Paris-Saclay, CNRS, ENS Paris-Saclay, CentraleSupélec, LuMIn UMR9024 & Inst. d'Alembert FR3242, 91190 Gif-sur-Yvette, France

robert.pansu@ens-paris-saclay.fr

Les déclins de fluorescence en phase solide sont très souvent complexes. Les solides ne sont jamais parfaits et les défauts sont la cause de quenching localisés. L'origine de la complexité est double.

- La vitesse du quenching dépend de la distance entre l'exciton et le quencheur. Or celle-ci est fixe et dispersée dans un solide.
- Le nombre de quencheurs dans le volume efficace de quenching est de l'ordre de quelques unités.

Cette complexité explique l'exploitation des déclins de luminescence soit très peu utilisée et mal théorisée.

Une approche robuste de l'exploitation des déclins de luminescence des solides est d'exploiter la linéarité qui existe entre la vitesse du déclin de la luminescence et la densité de défauts $< n >$: [1]

$$Ln\left(\frac{I_f(t)}{I_f(0)}\right) = -k_f t + < n > \left\{exp\left(\int_0^t k_{Q1}(u)du\right) - 1\right\} \quad \text{(eq 1)}$$

Pour cela il faut pouvoir moduler la densité de défauts. Pour les solides massifs cela peut se faire par irradiation avec des rayonnements pénétrants. Pour les suspensions de nano-particles, qui sont des solides dispersés dont la taille est plus petite que le volume efficace de quenching, cela se fait par addition de quencheurs à la suspension. Cette approche sera illustrée par des exemples.

Indépendamment du nombre de quencheurs, la cinétique elle-même peut être modélisée dans le cas du quenching de Förster et de Dexter. Le modèle du continuum qui remplace la présence ou l'absence d'un quencheur par sa probabilité de présence moyenne, malgré sa puissance de simplification, s'avère faux dans le cas de la fluorescence. En effet la dynamique de la mesure permet de voir distinctement la contribution des populations avec 0, 1 ou quelques quencheurs. Cette complexité n'empêche pas la linéarité de la vitesse du déclin avec concentration moyenne de quencheurs (eq 1). Nous proposons une nouvelle expression analytique pour les déclins de luminescence en présence d'un quenching de Förster.[2]

Cet échec du modèle du continuum est une conséquence de la nature moléculaire des excitons. Cela a été mis en évidence pour la première fois par les Perrin.[3]

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Copper-based Nanoparticles for CO2 Electroreduction

Y. Segura,[a,*] A. Amanova,[a] G. Montillet,[a] M. Huseynov,[a] P. Surut,[a] H. Remita,[a] L. Assaud,[b] and A. Ranjbari.[a,*]
[a] Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, Bât 349, 91405 Orsay, France

[b] Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182 CNRS, Université Paris Saclay, Bât 410-420, 91405 Orsay, France

yutzil.segura-ramirez@universite-paris-saclay.fr

alireza.ranjbari@universite-paris-saclay.fr

The electrochemical reduction of CO_2 (CO_2RR) supported by electrocatalysts is an alternative for the valorization of CO_2 into products of added value [1]. Copper-based materials exhibit good performance during the electrochemical conversion of CO_2 into different by-products such as carbon monoxide, methanol, methane, formaldehyde, and formic acid [2]. However, a problem of selectivity remains during this reaction. The combination and cooperation of metals have shown to increase the selectivity, activity, and stability of electrocatalysts, especially when they are presented in the form of nanomaterials [3]. Some of the advantages that such materials present, are the need for fewer electrocatalysts due to the increase of the surface area. In this work nanoparticles (NPs) synthesized via radiolysis were evaluated as electrocatalysts for the CO_2RR. The physicochemical characterization of the products was done via UV-Vis spectroscopy, XRD and SEM/EDS, while the electrochemical properties were characterized using cyclic voltammetry and EIS techniques. The products of the CO_2RR were identified using micro-GC and UV-Vis spectroscopy for the gas and liquid phases, respectively. Among the different compositions, CuPd NPs exhibited the best performance for the conversion of CO_2 into formic acid (HCOOH) in the liquid phase. Therefore, the use of bimetallic NPs led to an enhancement of the selectivity and activity of the electrochemical reaction since Pd increases the production of HCOOH and Cu decreases the production of H_{2n}. Results shed light on the synergetic effects of bimetallic catalysts for the valorization of CO_2.

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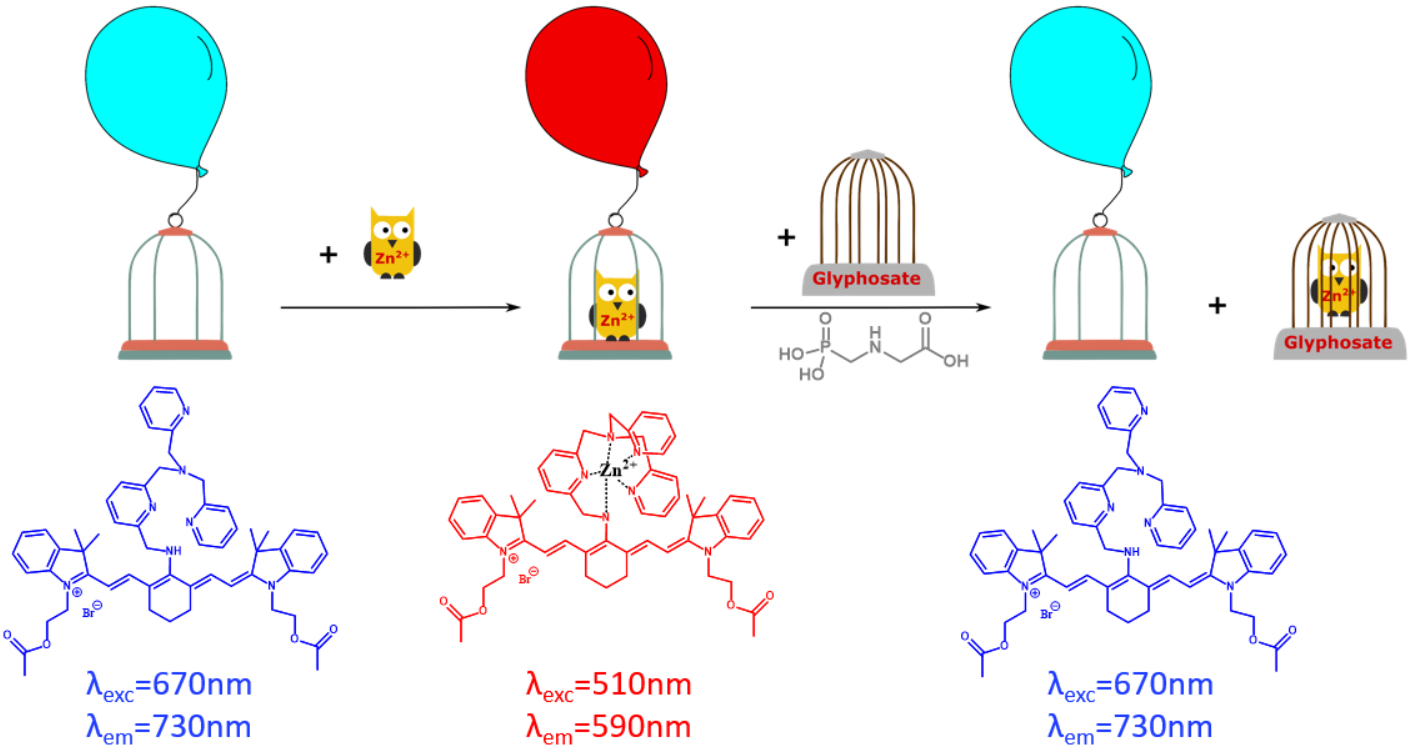
[2] Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F.; Chorkendorff. *Chem. Rev.* **2019**, *119* (12), 7610–7672.
[3] Talukdar, B.; Mendiratta, S.; Huang, M. H.; Kuo, C. *Chem. Asian J.* **2021**, *16* (16), 2168–2184.

Towards glyphosate optical sensor.

B. Amouroux,[a,b], I. Leray,[a] Gilles Clavier,[a] Ludivine Houel-Renault,[b] Rachel Méallet,[b] and Cédric Mongin[a]
[a] ENS Paris-Saclay, Université Paris-Saclay, CNRS, PPSM, 91190 Gif-sur-Yvette, France
[b] Institut Des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, 91405, Orsay, France
baptiste.amouroux@ens-paris-saclay.fr

While pesticides have been largely implemented for multiples purposes, their poisoning issue have made them a rising concern. Therefore, the development of accurate quantitative sensors to control pesticide poisoning combining high sensitivity and high selectivity has become a major stake [1]. We decided to address Glyphosate which is the most important herbicide used worldwide. However, routine detection remains limited due to the high cost required for each analysis and the conventional chromatographic approaches (LC/MS) [2] are not appropriate for field analyses and are highly time consuming. Various alternatives have been explored spanning from capillary electrophoresis, supramolecular chemistry, electrochemistry, to immunoassays; but they cannot reach satisfactory limit of detection and selectivity [3]. More recently, interesting competitive complexation and cation displacement strategies have been implemented [4]. Detection can be monitored using spectroscopic techniques with sub-ppm detection limit.

Thus, we decided to develop a fluorescent NIR probe (heptamethine cyanine), allowing background-free and fast detection, even in complex media. Thanks to the coupling of this dye with pyridine-based chelating moiety, our strategy focus on competitive metal cation binding of the probe compared to glyphosate. In the present poster will be reported the synthesis of the sensor and first complexation results.



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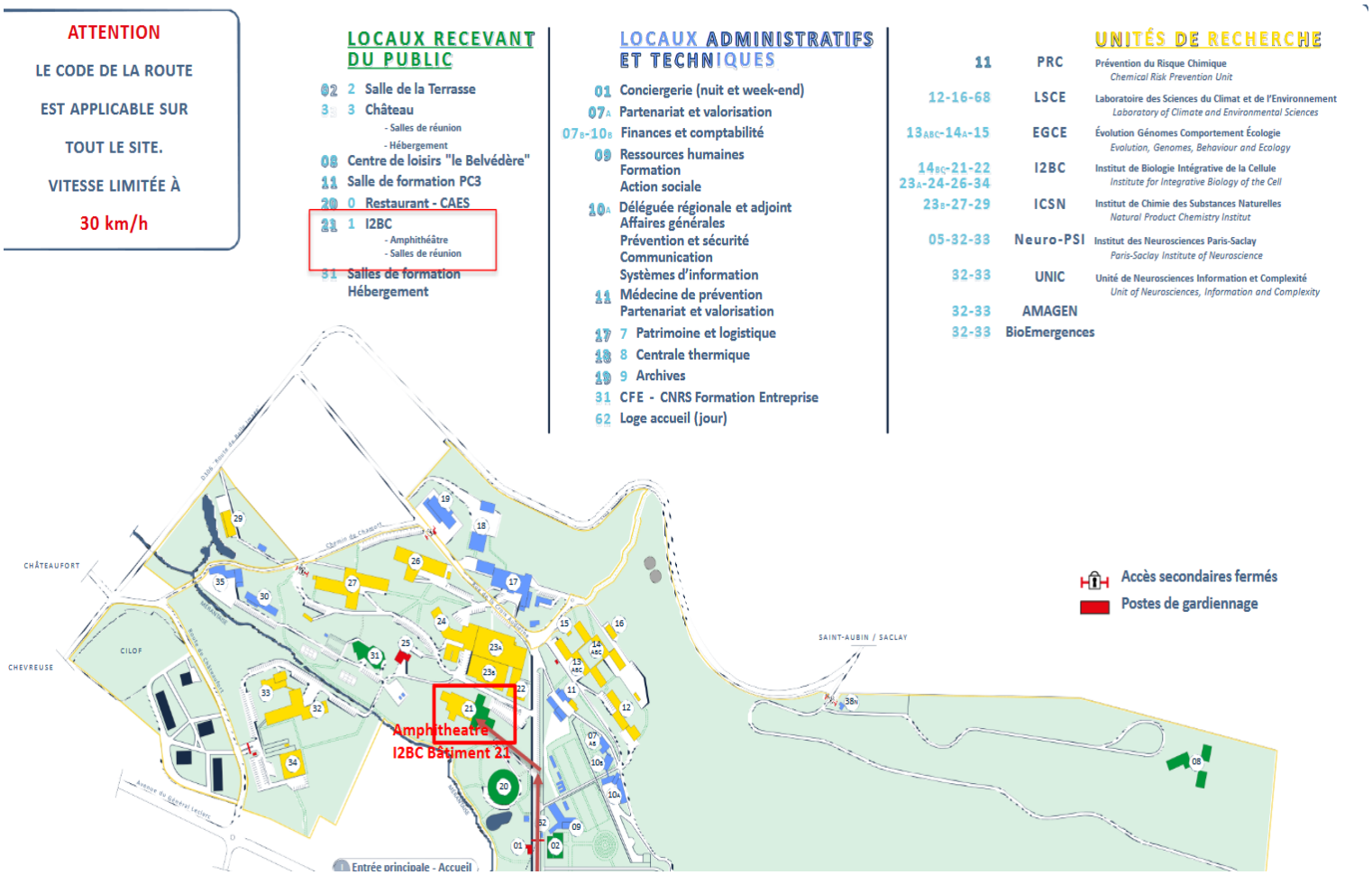
[4] Y. Sasaki, *et al.*, *Chem. Eur. J.*, **2020**, *26*, 14525



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