Journées plénières 2025
du GdR CNRS
PhotoElectroStimulation
(RT PES2)

27-28 Janvier 2025

Université de Strasbourg

Booklet of Abstracts

Université de Strasbourg

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Institut de Chimie de Strasbourg UMR 7177

Fondation Jean-Marie Lehn

GdR CNRS

PhotoElectroStimulation

(RT PES2)

Objectifs :

Le GDR PES2 aura pour mission de fédérer les communautés des électrochimistes, photochimistes, chimistes de synthèse et théoriciens autour des problématiques mettant en jeu une action conjointe de la lumière et des phénomènes d'injection ou d'extraction de charge et impliquant l'utilisation d'électrodes en présence de molécules ou matériaux stimulables. Les phénomènes concernés sont la photoélectrocatalyse, la conversion d'énergie électrique en énergie chimique (ou réciproquement) assistée par la lumière, la détection duale optique et électrochimique de processus biologiques, la commutation optique et électrochimique des propriétés de (nano)matériaux moléculaires et hybrides.

Conformément à l'esprit original, le GDR PES2 continuera d'organiser des manifestations scientifiques favorisant les échanges entre les membres de la communauté. Pour cette nouvelle mandature, il s'emploiera également à développer des actions de formation à destination des jeunes chercheur.ses et doctorant.es. et créer une ouverture vers l'international.

Axes :

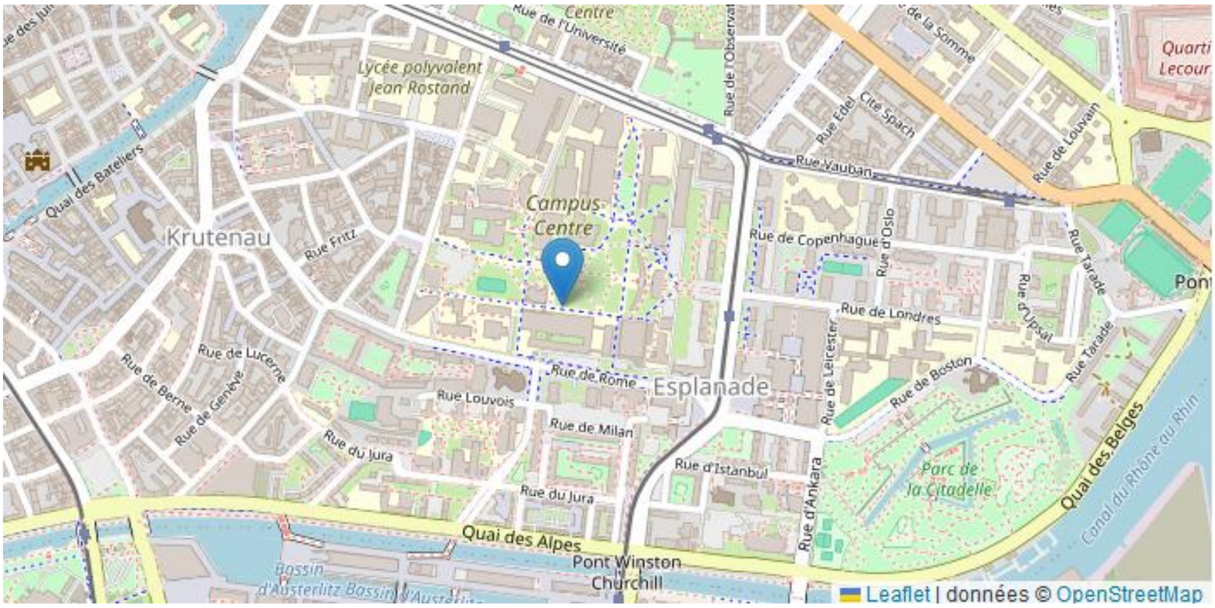
Ces missions seront déclinées selon 3 axes principaux :

1. Synthèse de molécules et matériaux photo- ou électrocommutables ;
2. Investigation des mécanismes impliqués dans les réactions couplant photons et électrons ;
3. Instrumentation couplant photochimie & électrochimie pour l'activation ; la détection ou le suivi de phénomènes d'origines chimiques ou biologiques.

Location

The plenary days of the GDR PES2 2025 will take place in the Salle des Thèses (Alain Beretz Amphitheater), located in the President's Building (Le Nouveau Patio), on the Esplanade campus of the University of Strasbourg.

Adress: Bâtiment de la Présidence Le nouveau Patio – Campus central Esplanade, 18 rue René Descartes, 67000 Strasbourg.



Access Plans for the GDR PES2 2025 Plenary Days:

From Strasbourg Train Station:

By Tram: Take **line C** towards **Neuhof Rodolphe Reuss** or **line E** towards **Campus d'Illkirch**. Get off at the **Université** or **Esplanade** stop (about 10 minutes).

By Bus: Several bus lines connect the campus to the city center. Please check the schedules on the CTS (Strasbourg Transport Company) website.

On Foot: The campus is a **25–30 minutes** walk from the train station.

Plenary sessions in Strasbourg

Monday, January 27, 2025

Hours	Event	Speaker	Communication title
13:00 - 14:00	Home - Welcoming participants		
14:00 - 14:10	Welcome - Laurent Ruhlmann		
14:10 - 14:20	Introduction - Fabien Miomandre, director of the GDR PES		
14:20 - 14:40	OC1[**]	Durin Gabriel	Experiment-Theory Synergy: Connecting the Kinetics of Molecular Catalysis of Electrochemical Reactions with Calculated Energy Landscapes
14:40 - 15:00	OC2	Cottineau Thomas	Local Photoelectrochemistry and Data Modeling for Operando Properties Extraction of Photoelectrodes
15:00 - 15:20	OC3	Bouffier Laurent	Towards high-resolution imaging of electrochemical processes by fluorescence laser scanning confocal microscopy
15:20 - 15:40	OC4	Jiang Ning	Electrochemical and Chemical Switching Fluorescence Emission in Ferrocene-Rhodamine Dyads
15:40 - 16:00	OC5	Miomandre Fabien	Plasmon-mediated fluorescence switch under electrochemical control
16:00 - 16:30	**Coffee break**		
16:30 - 16:50	OC6	Rogez Guillaume	Multifunctional Layered Hydroxides and Oxides for Magnetic, Luminescent or Electrocatalytic Properties
16:50 - 17:30	PC1[*]	Filhol Jean-Sébastien	Ab initio electrochemistry applied to (energy) materials
17:30 - 17:50	OC7	Molinaro Céline	Photopolymerization or thermopolymerisation selectively induced through controlled plasmonic excitation of gold nanoparticles
17:50 - 18:10	OC8	Groslambert Geoffrey	Electroresponsive hydrogels from supramolecular polymers
18:10 - 19:00	**Cocktail (free for the participants)**		
20:00 - 22:30	**Dinner**		

Tuesday, January 28, 2025

09:00 - 09:40	PC2	Loubiere Karine	Flow photochemistry: a chemical engineering perspective
09:40 - 10:00	OC9	Bui Anh Thy	Lanthanide-based TADF dyes
10:00 - 10:20	OC10	Hoffmann Norbert	Photochemical reactions of oxazolones – Insights in the reaction mechanism
10:20 - 10:50	**Coffee break**		
10:50 - 11:10	OC11	Akhsassi Brahim	Covalent Polyoxometalate – polyporphyrin systems for photo(electro)catalysis
11:10 - 11:30	OC12	Mialane Pierre	Roles of polyoxometalates in the photocatalytic CO2 reduction reaction
11:30 - 11:50	OC13	Dawoud Samer	Photoelectroactive covalent hybrids based on (iso)porphyrin-polyoxometalate assemblies
11:50 - 12:10	OC14	Tlaiss Mariam	Photochromism of novel electropolymerized systems that combine diarylethene and porphyrin moieties: studied with using Spectroelectrochemistry and Ultrafast Absorption Spectroscopy
12:10 - 14:00	**Lunch at the Brasserie Le 32 Restaurant (free for the participants)**		
14:00 - 14:20	OC15	Jacquot de Rouville Henri-Pierre	The Viridium Radical Cations
14:20 - 14:40	OC16	Ishow Eléna	Cooperative photoswitching materials
14:40 - 15:00	OC17	Nakatani Keitaro	Amplified switching by cascade reaction in photochromic terarylenes
15:00 - 15:20	OC18	Aloise Stéphane	Easy processable photomechanical thin film involving a photochromic diarylethene and a thermoplastic elastomer in supramolecular interaction
15:20 - 15:30	Oral communication awards		
15:30 - 16:00	**Coffee break & Departure**		

***PC: Plenary Conference**
****OC: Oral Communication**

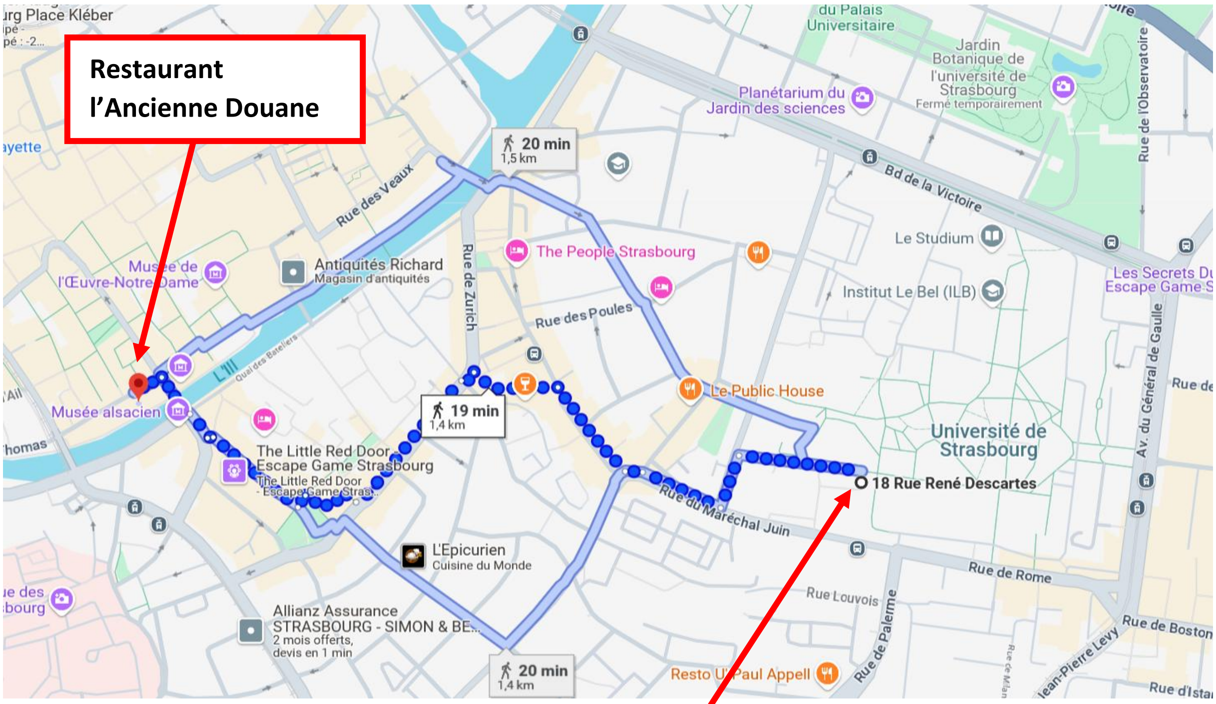
Diner du Lundi 27 Janvier / Dinner Monday 27 January 2025

(Membres extérieurs à l'université de Strasbourg invités / Guest members from outside the University of Strasbourg) :

Restaurant l'Ancienne Douane à 20 :00

6 rue de la Douane, 67000 Strasbourg

https://www.anciennedouane.fr/



Restaurant l'Ancienne Douane

Salle des Thèses (Amphithéâtre Alain Beretz),

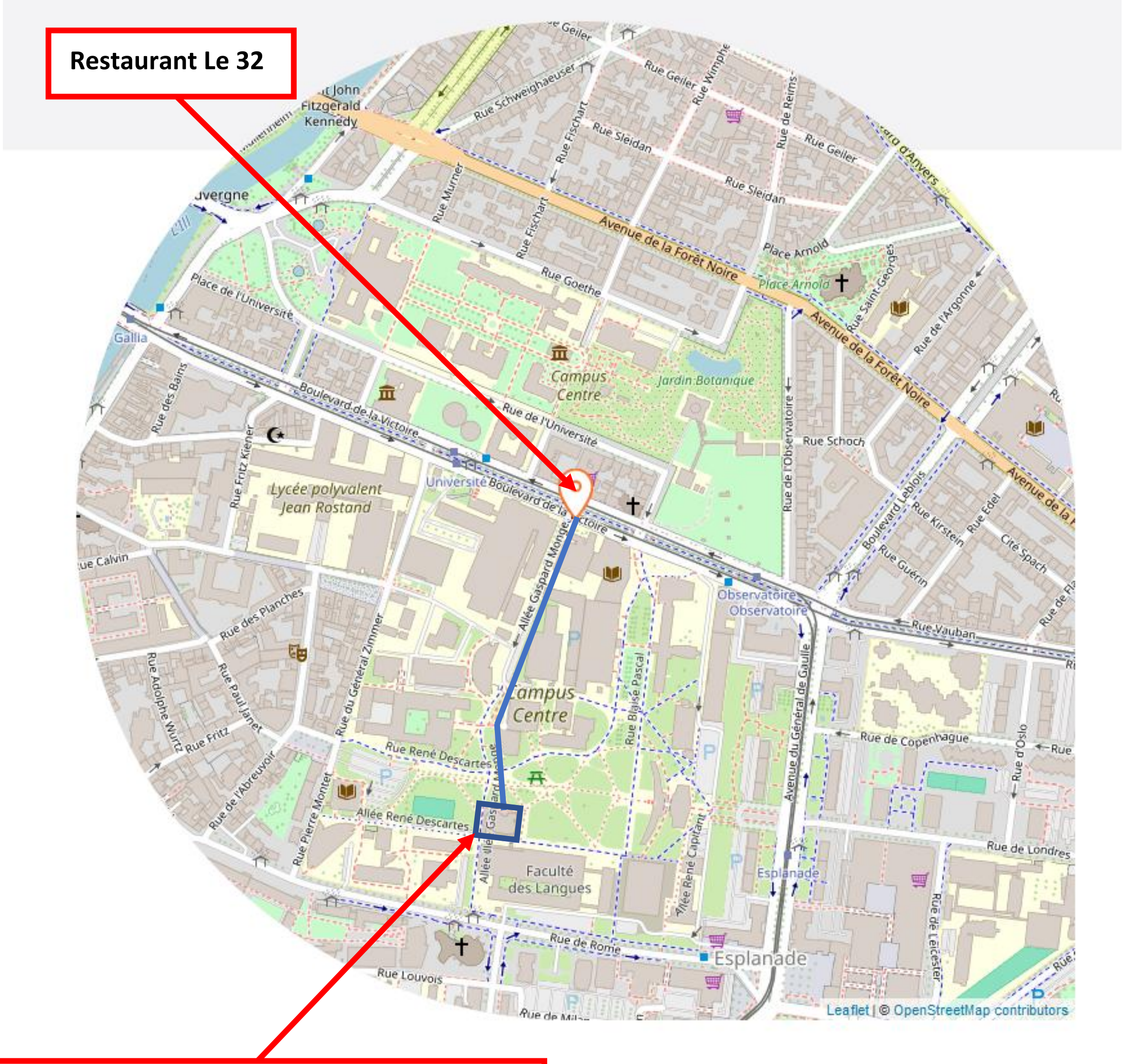
Bâtiment de la présidence (Nouveau Patio)

Déjeuner du Mardi 28 Janvier :

Restaurant Brasserie Le 32 (derrière étage du CROUS de l'Esplanade)

32 boulevard de la Victoire, 67000 Strasbourg

https://www.crous-strasbourg.fr/restaurant/le-32-2/



Restaurant Le 32

Salle des Thèses (Amphithéâtre Alain Beretz),

Bâtiment de la présidence (Nouveau Patio)

Booklet of Abstracts

Plenary Lectures

Ab initio electrochemistry applied to (energy) materials

Jean-Sébastien Filhol, L. H. B. Nguyen, A. Kopač Lautar, A. Hagopian, M.-L. Doublet, H. Guesmi

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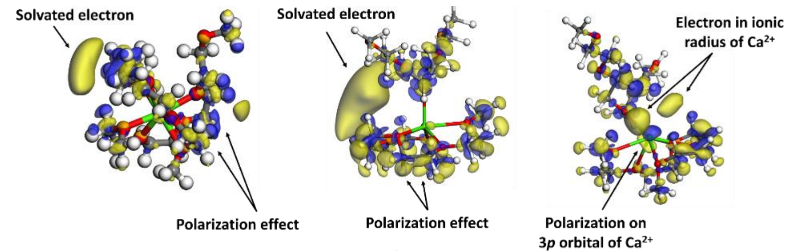
Modeling electrochemical processes, especially at interfaces, is essential for understanding the complex reactions involved in energy conversion and storage. Since Marcus's foundational work, the relationship between solvation and redox processes at metal anodes has been increasingly understood.[1] However, traditional models have largely relied on semi-empirical methods. To advance this field, we have developed an ab initio approach that incorporates electrode potential effects and solvation at the atomic scale, enabling the modeling of complex battery processes such as dendritic growth, electrolyte degradation, and cation reduction, as well as catalytic processes for fuel production in energy conversion systems.

We first illustrate how this approach redefines our understanding of dendritic growth that is one of the problematic effects preventing an easy use of metal anodes. We then present our findings on electrode-interface degradation processes that lead to the formation of the solid electrolyte interphase (SEI) for various metal anodes (e.g., Li, Mg, Ca) using our approach.[2] Our results reveal that redox processes within the electrochemical double layer are highly intricate, often involving solvent[4,5] or ion[6] reduction. This behavior, which leads to electrolyte decomposition into degradation products, is attributed to electrophilic activation by the metal cations. Nevertheless, this degradation can be mitigated by incorporating carefully selected additives with protective functions.[7] For alkali earth cations reduction efficiency is shown to be even more complex, resulting from a delicate balance between electron transfer, solvent reorganization, and electrolyte reactivity Our study demonstrates for example that reducing Ca^{2+} cations at electrochemical interfaces requires a reduction of the number of coordinated solvent molecules, which permits a transition from a solvated electron-cation pair to a reduced cation.[9] This suggests that metal cation reduction at electrochemical interfaces is more intricate than currently understood and has far-reaching implications for electrochemical applications from batteries to metal plating. Finally, we will show how this approach can be extended to other fields of energy materials such as fuel cells or fuel electro-catalytical production giving some new insights in the complexity at the associated interfaces.

References:

1) R. A. Marcus J. Chem. Phys. 24 (1956) 966.
2) A. K. Lautar, A. Hagopian and J.-S. Filhol Phys. Chem. Chem. Phys. 2020, 22, 10569-10580
3) A. Hagopian, M.-L. Doublet and J.-S. Filhol Energy Environ. Sci. 2020, 13, 5186-5197
4) N. Lespes and J.-S. Filhol J. Chem. Theory Comput. 2015, 11, 3375-3382
5) A. Kopač Lautar, J. Bitenc, T. Rejec, R. Dominko, J.-S. Filhol and M.-L. Doublet J. Am. Chem. Soc. 2020, 142, 5146-5153
6) L. H. Nguyen, T. Picard, C. Iojoiu, F. Allouin, N. Sergent, M. L. Doublet and J.-S. Filhol Phys. Chem. Chem. Phys. 2022, 2201417
7) A. Kopač Lautar, J. Bitenc, R. Dominko and J.-S. Filhol ACS Appl. Mater. Interfaces 2021, 13, 8263-8273Phys. Chem. Chem. Phys. 2022, 2201417
8) L. H. B. Nguyen and J.-S. Filhol, Adv. Energy Mater. 2023, 13, 2300311



Evolution of a reduced solvated Ca^{2+} cation as function of the solvation

Flow photochemistry: a chemical engineering perspective

Karine Loubière

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Organic photochemistry is a key synthetic pathway for sustainable chemistry. Multistep syntheses of complex molecules are shortened and simplified, a portfolio of novel chemicals becomes accessible, and the photon acts as a "traceless reagent" [1]. Several fundamental principles of green chemistry are thus addressed by photochemistry. The implementation of organic photochemistry at an industrial scale remains however limited to a few examples in bulk chemistry or fine/specialty chemistry [2]. Batch reactors equipped with energy-demanding light sources are the systems currently used for industrial photochemical processes.

Continuous-flow microstructured technologies, which involve channels or tubes from tens of micrometers to a few millimeters in diameter, are now recognized as alternatives to batch processing. Their benefits for organic photochemistry have been highlighted more recently [3-4]. The integration of light emitting diodes (LEDs) as light sources in these technologies provides new opportunities.

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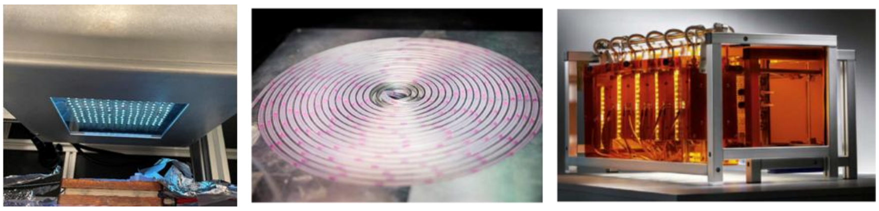

The present communication will start with some general considerations of preparative photochemistry. Secondly, the advantages of continuous-flow microstructured technologies for photochemistry will be described, in particular when combining with LEDs as selective and efficient light sources. From this, the challenges for implementing chemical engineering frameworks will be discussed with the prospect of developing generic strategies able to define the optimal conditions when operating photochemical reactions, to address batch-to-continuous transfer and smart-scale-up issues. Lastly, some illustrative examples will be shown, including (i) the comparison between batch and continuous-flow processes in the case of a [2+2] intramolecular photocycloaddition [5], (ii) the study under continuous-flux conditions of a sensitized photooxygenation depending whether free sensitizer or photoactive colloids are used [6], and (iii) the batch-to-continuous transfer of the photochemical reaction of an oxazolone derivative in an advanced UVC-LED-driven microreactor [7].

References:

[1] Hoffmann, N. *Chem. Rev*. **2008**, 108 (3), 1052–1103.

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[4] Loubière K., Oelgemöller M., Aillet T., Dechy-Cabaret O., Prat, L. *Chem. Eng. Process*. **2016**, 104, 120132.

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Booklet of Abstracts

Oral Communications

Experiment-Theory Synergy: Connecting the Kinetics of Molecular Catalysis of Electrochemical Reactions with Calculated Energy Landscapes.

Durin G. (1), Costentin C.* (1)

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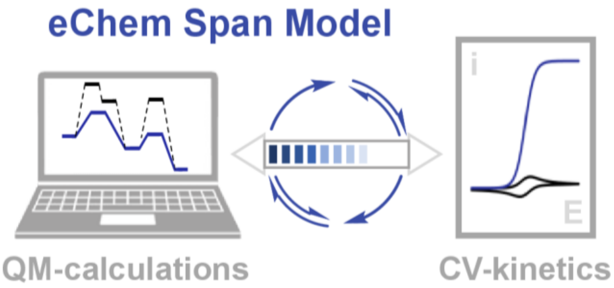
The electrification of processes is a challenge for transitioning away from fossil resources. Catalysis plays an essential role in the efficiency of these processes (e.g. rate, energy input, selectivity). Molecular catalysis stands out for its ability to study in detail the mechanisms involved in these transformations, thanks in particular to the well-defined nature of these homogeneous catalysts. A particularly effective approach to understanding these mechanisms is to compare experimental results with calculated energy landscapes. Such synergy has already proved its worth in thermal molecular catalysis, notably *via* the 'span model'.[1] However, this approach is still in its infancy in the molecular catalysis of electrochemical reactions. Calculated energy profiles are rare and often lack experimental kinetic validation due to limited kinetic data or ambiguities linking calculated and experimental observables (e.g. inconsistent reaction order, large TOF discrepancy).

Here we extend the 'span model' to electrochemical reactions catalysed by molecules, focusing on traditional EC_1 ...C□E' mechanisms (**Scheme 1**).[2] We thus establish a framework for aligning theoretical estimates of turnover frequency with practical measurements of cyclic voltammetry in electrochemical systems, that account for complexities in the diffusion-reaction layer. The analysis also identifies specific kinetic zones, defining the conditions under which different catalyst intermediates dominate the diffusion-reaction layer. This model is then applied to the experimentally well-studied electrochemical reduction of CO_2 to CO using an iron tetraphenylporphyrin catalyst and phenol as proton donor.[3] These results allow us to discuss the challenges of predicting the behaviour of catalysts in the reaction diffusion layer. Overall, this approach helps to refine the 'span model' for electrochemical catalysis and can improve the alignment of experimental data with theoretical calculations, towards a mechanistic consensus.



Scheme 1. *Transposition of the 'span model' of molecular thermal catalysis to electrochemical reactions*

References:

[1] Kozuch, S.; Shaik, S. How to Conceptualize Catalytic Cycles? The Energetic Span Model. *Acc. Chem. Res.* **2011**, *44*, 101-110, https://doi.org/10.1021/ar1000956

[2] **Durin, G.**; Costentin C. *ACS Catal.* **2025** (accepted)

[3] Tarrago, M.; Ye, S.; Neese, F. Electronic structure analysis of electrochemical CO_2 reduction by iron-porphyrins reveals basic requirements for design of catalysts bearing non-innocent ligands. *Chem. Sci.* **2022**, *13*, 10029-10047, http://dx.doi.org/10.1039/D2SC01863B

Local Photoelectrochemistry and Data Modeling for Operando Properties Extraction of Photoelectrodes

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Recent advances in materials science have opened up great opportunities for the design of heterostructures associating two or more components that could lead to highly efficient photoelectrodes usable for photoelectrochemical (PEC) solar to chemical energy conversion. However, in these heterostructures, any change in morphology or composition will impact all steps of the PEC reaction,[1] making the quest for the best materials and structures a difficult process. Therefore, to assist in the rational design of PEC devices, there is an urgent need for characterization methods to rapidly determine the properties of photoelectrode materials and understand how any structural or physicochemical changes impacts the PEC efficiency. Until now, the optimization of photoelectrodes in terms of material composition, film thickness, or co-catalyst loading is still largely achieved through a trial-and-error approach by synthesizing and analyzing a set of different electrodes, which can be time and resource-consuming.[2]

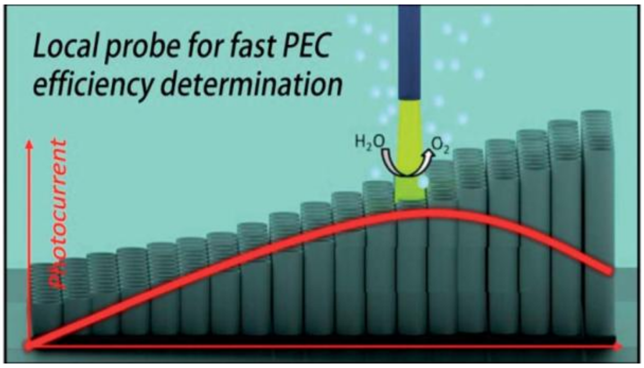

Figure 1: *principle of the local probe PEC measurement on variable NTs length electrode.*

Here we will present a new analytic approach based on local PEC efficiency measurement using a small light beam as a local probe to scan the surface of photoelectrode with variable properties. We developed a new approach that allows the growth of aligned TiO_2 nanotubes (NTs) with length increasing gradually from 0 to 15 µm, on a single electrode.[3] This method was employed to synthesize TiO_2-NTs with variable length but also doped TiO_2-NTs with cations (Nb, Ta) and/or anions (N).[4] Therefore, with one synthesis and one PEC measurement, we were able to determine the optimal length of the NTs for PEC applications. The experimental data for the different samples shows different behaviors that can be ascribed to changes of electronic conductivity and light absorption depending on the doping species. By modelling these data, some important parameters of the photoelectrode, such as charge transfer, absorbance or electron mobility, were determined directly from the local PEC measurements.[5]

References

[1] K. Takanabe, ACS Catalysis. 2017, 7, 8006.
[2] W. Yang, R.R. Prabhakar, J. Tan, S.D. Tilley, J. Moon, Chem. Soc. Rev.2019, 48, 4979.
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[4] T. Favet, V. Keller, M. A. El Khakani, T. Cottineau, Material Today Energy, 37, 2023, 101376
[5] S. Vergne, F. Gelb, V. Keller, T. Cottineau, Solar RRL 8, 2024, 2400156

Towards high-resolution imaging of electrochemical processes by fluorescence laser scanning confocal microscopy

Wu X. (1), Dauphin A. (1), Goudeau B. (1), Longatte G. (1), de Poulpiquet A. (2), Sojic N. (1), and **Bouffier L.*** (1)

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The coupling between electrochemistry and fluorescence microscopy is gaining a major renewal of interest. This is due to the high level of space- and time-resolved information that can be achieved by collecting simultaneously these two analytical signals, uncovering spatial or temporal heterogeneities of electrode processes [1-3].

During the past decade, we have implemented fluorescence confocal laser scanning microscopy under electrochemical control in order to map either in 2D (in-plane of the electrode surface) or in 3D (away from the electrode surface) various reaction layers associated with interfacial electron transfer processes. [4,5]

In this contribution, the comparison between large scale macroelectrodes and much smaller microelectrodes will be used to address the limit of resolution that can be reached [6]. In particular, the high-resolution imaging of microscale opto-electrochemical arrays based on optic fibre bundles will be demonstrated [7]. For example, the figure below gathers a top view (a), an orthogonal view (b) and a 3D reconstruction (c) of a high-density array of microtips).

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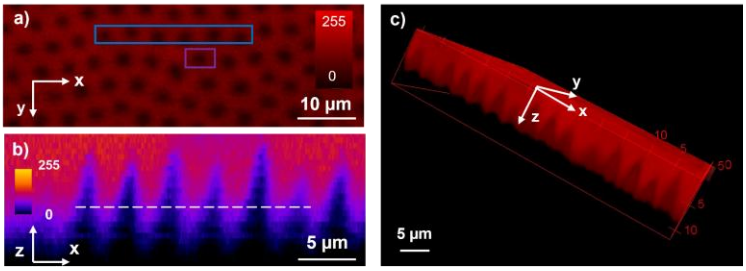

References:

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[7] X. Wu, A. L. Dauphin, B. Goudeau, G. Longatte, N. Sojic, L. Bouffier, *in preparation*.

Electrochemical and Chemical Switching Fluorescence Emission in Ferrocene-Rhodamine Dyads

Ning Jiang (1), Carolina Chieffo (2), Blaise Dumat (2), Jean-Maurice Mallet (2),
Eric Labbé (1) and Olivier Buriez * (1)

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The design and development of molecules whose fluorescence can be switched as a function of their redox state is a very attractive approach in analytical and bioanalytical chemistry since many analytes are redox active and can be detected and/or mapped with high sensitivity through fluorescence [1, 2]. Nowadays, the most effective strategy to tune fluorescence is based on the development of dyads in which an internal electron transfer or an energy transfer between a redox-active system and a fluorescent core can be enabled or forbidden [3, 4]. Within this context, we recently designed and synthesized an original ferrocene-appended rhodamine complex (see Figure) whose photo-physico-chemical properties were investigated by cyclic voltammetry, UV-Vis, and fluorescence [5]. Interestingly, the fluorescence quantum yield of the starting rhodamine derivative dropped drastically after clicking the ferrocene unit due to a photo-induced electron transfer. However, emission of the complex could be recovered upon electrochemical or chemical oxidation of the ferrocene part. Furthermore, the ferrocene-rhodamine complex underwent on/off switching between fluorescent and nonfluorescent states repeatedly.

This work provides new insights into the development of biocompatible reversible fluorescent probes especially for the detection of reactive oxygen and nitrogen species.

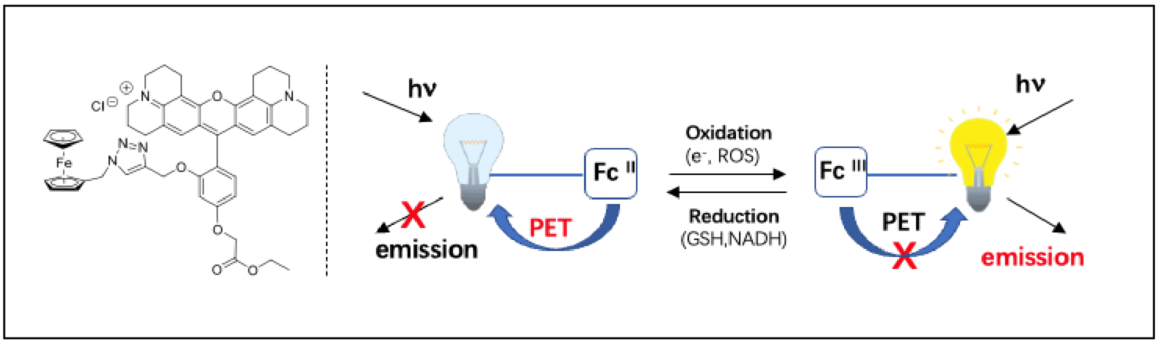

Figure. Schematic illustration of the fluorescence modulation in the dyad system of ferrocene-rhodamine structure and redox response.

References:

[1] F. Miomandre. *Curr. Opin. Electrochem.* **2020**, *24*, 56–62.
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[5] Unpublished results.

Plasmon-mediated fluorescence switch under electrochemical control

B. Maillot, A. Dabbous, J.F. Audibert, V. Brasiliense, and **F. Miomandre**.* (1)

(1) PPSM, ENS Paris-Saclay, CNRS, 4 avenue des sciences, 91190 GIF SUR YVETTE (France)

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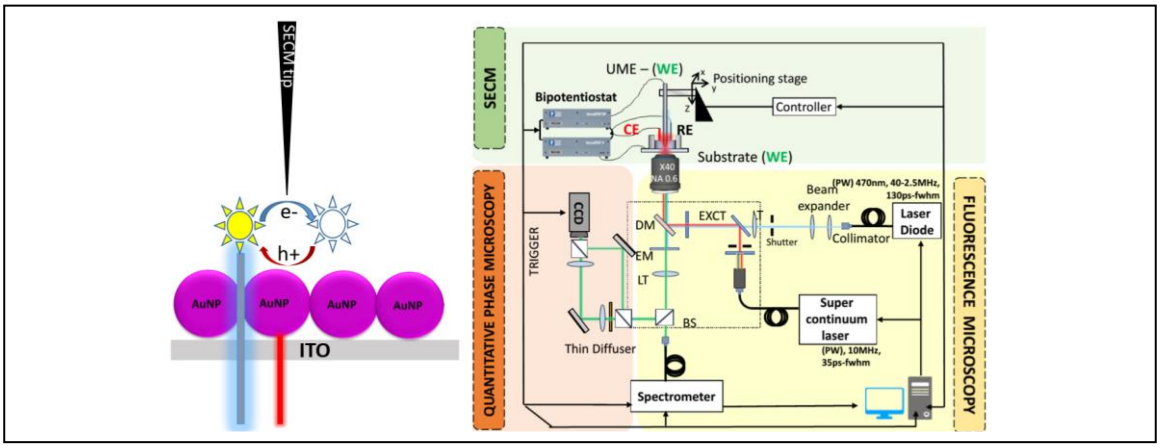
Plasmonic-activated electrochemistry is becoming a high-interest topic as it opens the way of using visible light to trigger or to boost redox reactions at the interface of nanoparticles[1]. Applications in the field of electrocatalysis are already in progress[2]. Nevertheless, the mechanisms involved in plasmonic activation (namely charge injection, heating and electric field enhancement) remain the topic of debates and are often entangled in practical uses.

To better understand these aspects, which is crucial to find conditions where one of them is favoured (here charge injection), we propose to use an electrofluorochromic probe and the simultaneous electrochemical and optical detections in a combined electrochemical and fluorescence microscope (see scheme below). Using first the probe in solution and then directly grafted on the nanoparticle surface, we have demonstrated that plasmonic activation proceeded by hole injectrion, an unexpected result in relation to the electron acceptor character of the probe. This results in a fluorescence switch which is monitored in a dual mode by the electrochemical signal at the tip and the laser excitation at the substrate[3].



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Multifunctional Layered Hydroxides and Oxides for Magnetic, Luminescent or Electrocatalytic Properties

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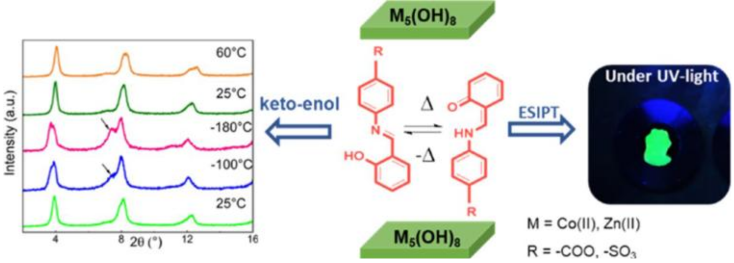
Multifunctional materials hold immense promise for applications as they offer a unique combination of physical, chemical, or mechanical properties. One possible approach to obtain such materials consists in associating two components, organic and inorganic, within a single hybrid material which thus may inherit the individual properties of its constituents as well as possess a new property due to a synergistic interaction between the properties.[1] For this hybridization purpose, layered compounds are candidate of choice, for the various compositions they can offer, the different synthetic approaches that are available and the different kinds of interactions between the two subnetworks that can be designed.[2–4]

In this presentation, I will focus on two different families of layered hybrid materials, layered simple hydroxides of general formula $M_x(OH)_{2x-yn}(X^{n-})_y$ (M(II) = Co, Ni, Cu, Zn and X being a carboxylate, sulfonate, sulfate or phosphonate ligand) and layered oxides with a perovskite structure (Dion-Jacobson or Ruddlesden-Popper phases) functionalized by amines or alcohols of formula $(R\text{-}NH_3)_xH_{1-x}LaNb_2O_7$, $(R\text{-}NH_3)_xH_{2-x}Bi_{0.1}Sr_{0.85}Ta_2O_7$, $(R\text{-}O)_xH_{1-x}LaNb_2O_{7-x}$ or $(R\text{-}O)_xH_{2-x}Bi_{0.1}Sr_{0.85}Ta_2O_{7-x}$.

In addition to synthetic aspects, ion-exchange, *in situ* post-synthesis modification and micro-wave activated reactions, I will present different examples of properties which can be reached in these materials.

In layered hydroxides, I will show how they can be designed for electrocatalysis applications, either for O_2 reduction,[5] or for CO_2 reduction,[6] or functionalization by photo and thermoresponsive salicylidene aniline (anils) derivatives (Scheme 1).[7]



Scheme 1. Functionalization of layered hydroxides by anils derivatives.

Finally, for layered oxides, I will describe our ongoing work on the design of new luminescent hybrid materials, associating the emission from the inorganic host, and the one from the organic or rare-earth guests.

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Photopolymerization or thermopolymerisation selectively induced through controlled plasmonic excitation of gold nanoparticles

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Localized surface plasmon induced polymerization of free-radical acrylate monomers is an efficient, smart, and versatile method for preparing metal/polymer hybrid nanoparticles (NPs) with accurate control of the thickness and spatial distribution of the polymer on the NP surface. Through decay processes, the plasmon emits light, hot charge carriers and heat (i.e. thermoplasmonic). While the photochemical pathway has already been used for generating hybrid NPs, thermoplasmonic effects have not been used in this context.

Here, we investigated the photochemical and the thermoplasmonic routes to graft polymer onto various colloidal gold NPs. Either pathway is selectively addressed using a specific formulation, either photopolymerizable (containing a photo-initiator) or thermopolymerizable (containing a thermal initiator). The plasmon is excited by fs-pulsed laser illumination at 800 nm (Ti:Saph). Samples are prepared directly on TEM (Transmission Electron Microscope) grids to observe the polymer with nanometric resolution.

In the case of photopolymerization, the spatial distribution of the polymer obtained enables the NP's electric field to be visualized for geometries with strong field localization, such as nanorods and nanotriangles (Fig. 1 b). In the case of nanodisks and hexagons, with less field localization, a continuous polymer layer is observed (Fig. 1a). [1]

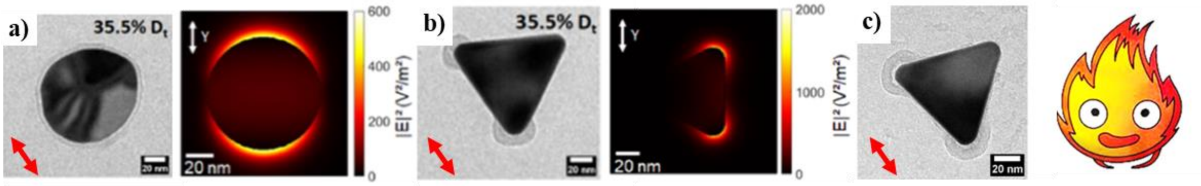

Figure 1: TEM images associated with field intensity map showing photopolymerisation [1] at the vicinity of a a) nanodisk, b) nanotriangle and c) thermopolymerization at summits of a nanotriangle. [2]

In the case of thermopolymerization, a specific formulation with a threshold polymerization temperature of 130°C has been developed and characterized in thermoplasmonics in the context of dense gold NP samples. [3] This formulation shows no absorption in the visible range, ruling out any photopolymerization mechanism. Surprisingly, we observed that the thermal polymer does not form a continuous layer around the triangle. This thermal polymerization, present in a localized pattern on the nanotriangle, highlights a non-homogeneous temperature distribution in this structure that can be mapped by our thermopolymerizable formulation.[2]

We have demonstrated here that fine control of these two phenomena will pave the way for new nanofabrication processes, which by photochemical or thermal means will make it possible to generate hybrid NPs with nanometric resolution.

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Electroresponsive hydrogels from supramolecular polymers

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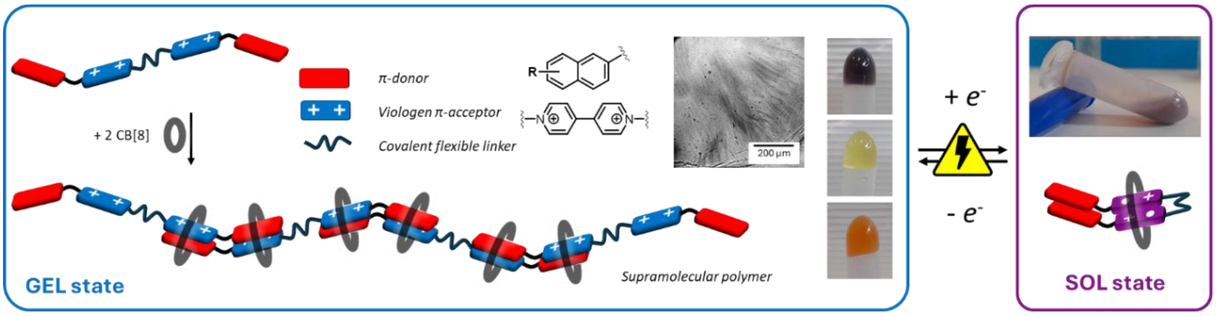
Interest in stimuli-responsive self-assembled soft materials has grown over the last decade. Hydrogels, in particular, have been the subject of extensive research because of their many potential applications.[1] Gels can be defined as solvent trapped in a network that typically contribute little to the mass. An important feature of supramolecular gels, involving a network of non-covalent bonds, is their ability to undergo self-healing processes or to respond to external stimuli (pH, T, P, light). These dynamic and stimulable soft materials have proved useful in many fields, from catalysis to electronics.[2]

Our project aims at addressing two challenges in the field of responsive hydrogels in line with the following observations: 1) Most stimuli- responsive behaviors reported so far come from serendipitous finding due to a lack of control and anticipation over the molecular events involved in the gelification process; 2) Responsiveness to electrical stimuli remains almost unexplored, despite being essential to ensure implementation of such materials in devices. our group has developed strong expertise in the characterization and engineering of electro-switchable gels.[3-6]

This presentation will focus on supramolecular gels formed by the spontaneous self-assembly of cucurbit[8]urils host with π-conjugated donors and electron-responsive bipyridinium acceptors.[7] The mechanisms of formation and response to stimulation will be discussed on the basis of spectroscopic, rheological, microscopic and electrochemical data of the hydrogels formed.



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Lanthanide-based TADF dyes

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Rare earth-containing materials are ubiquitous in diverse applications, luminescence-based purposes accounting for about a third of their uses.[1] The search for structures with optimal properties for detection, sensing or lighting for instance, has led to general design rules to optimize luminescence emission in lanthanide complexes, taking advantage of their spectrally sharp and long-lived metal-centered emission.[1,2] In this contribution, we will discuss situations where the complex can undergo reverse energy transfers to an organic chromophore,[3] a scenario that is usually undesired due to its efficiency in deactivating the lanthanide core. By tackling the problem from the organic dye standpoint, we will evidence unusual and intriguing photophysical behaviors that lead to new families of TADF (thermally activated delayed fluorescence [4]) emitters. This discovery is expected to open the way for lanthanide-based OLED devices that are poised to outperform existing TADF materials.

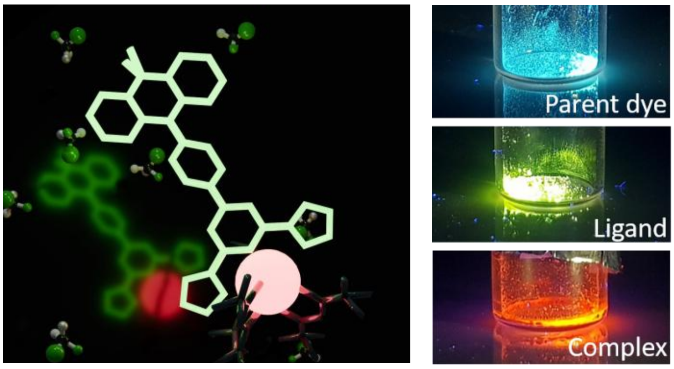

Figure. *Left: artistic representation of a lanthanide complex.*
Right: pictures of luminescent powders of TADF dyes under 365 nm irradiation

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Photochemical reactions of oxazolones – Insights in the reaction mechanism

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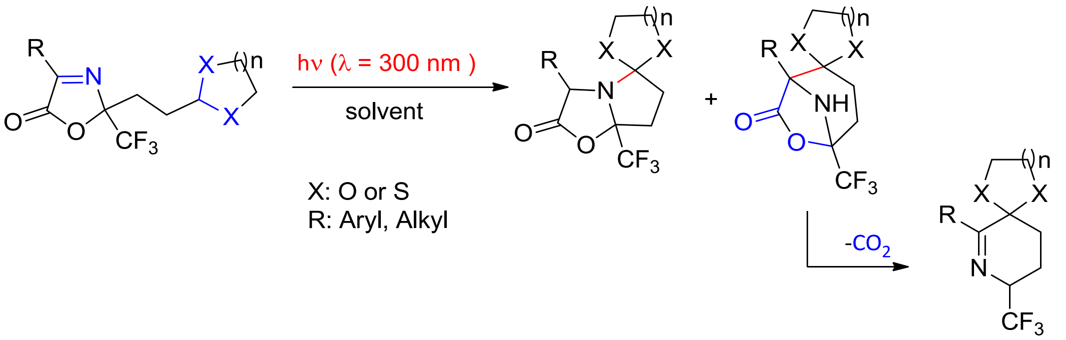
Photochemical intra- and intermolecular electron and hydrogen transfer lead to unusual products using a green chemistry method of organic synthesis.[1,2] Such reactions play an important role in the organic synthesis as they generate heterocycles with a high degree of molecular complexity and diversity which makes them interesting for application to the synthesis of biologically active compounds.

Physicochemical investigations provide a profound understanding of such processes. Our recent research in this domain deals with photo-induced intramolecular hydrogen transfer in oxazolones possessing an imine function (Scheme).[3] Acetale or thioacetale functions on the side chain are hydrogen atom donors. We are particular interested in the regioselectivity of these reactions. Triplet diradical intermediates are formed. After intersystem crossing the final products are obtained. A (C-C)- or a (C-N)-bond is formed. The regioselectivity is determined in the last step by the intersystem crossing mode [4] and the structure of the singlet state. The rate of the decarboxylation depend on the substitution pattern. The reaction has also been performed using continuous flow conditions.[5]



Scheme. Intramolecular reactions of oxazolones involving photo-chemically induced hydrogen atom transfer.

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Covalent Polyoxometalate – polyporphyrin systems for photo(electro)catalysis

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The development of hybrid materials incorporating polyoxometalates (POMs) is a promising approach to elaborate new functional materials. To expand the practical applications, their association to a visible-light photosensitizer is needed and has been explored (Fig. 1). In particular, the development of hybrid polymers incorporating POMs is a promising approach to elaborate new functional materials. Different strategies have been developed and explored. One approach consists in the entrapment of POMs in polymeric networks or the sandwiching of POMs between cationic polymers in layer-by-layer assemblies. In a second approach, coordination polymers were formed from polyoxometalates and organic ligands to yield new oxide materials with various structures, such as 1D chains, 2D networks, and 3D frameworks. In the third approach, we have developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin radical cation or dications [1]. The formation of hybrid POM-porphyrin copolymeric films can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Py-POM-Py) [2]. This process is feasible for various type of POMs [3-5] or cluster [6-10] such as Dawson, Lindqvist, Anderson or Keggin type POMs.

Stable isoporphyrin – POM copolymers (POM = Dawson or Anderson) have been also develop recently showing interesting efficiency even upon the NIR illumination. Such materials will be compared with other porphyrin-POM compounds using various type of POMs. The photovoltaic performances of these hybrid materials have been investigated under visible-light illumination given by now good efficiency (Figure 1). The impedance as well as photochemical properties of such hybrid material under visible or NIR illumination will be also discussed. Their application in photocatalytic metal ions (Ag^+, $Au^{III}Cl_3^-$, $Pt^{IV}Cl_6^{2-}$) reduction has been also studied showing high efficiency.

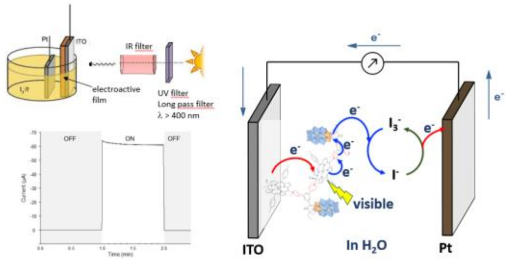

Fig. 1. Energy level diagram for electropolymer $[IsoZnT_2P\text{-}Py^+\text{-}POM\text{-}Py]_n$- (POM = Dawson) ($Py^+$ = pyridinium, isoP = isoporphyrin).

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Roles of polyoxometalates in the photocatalytic CO_2 reduction reaction

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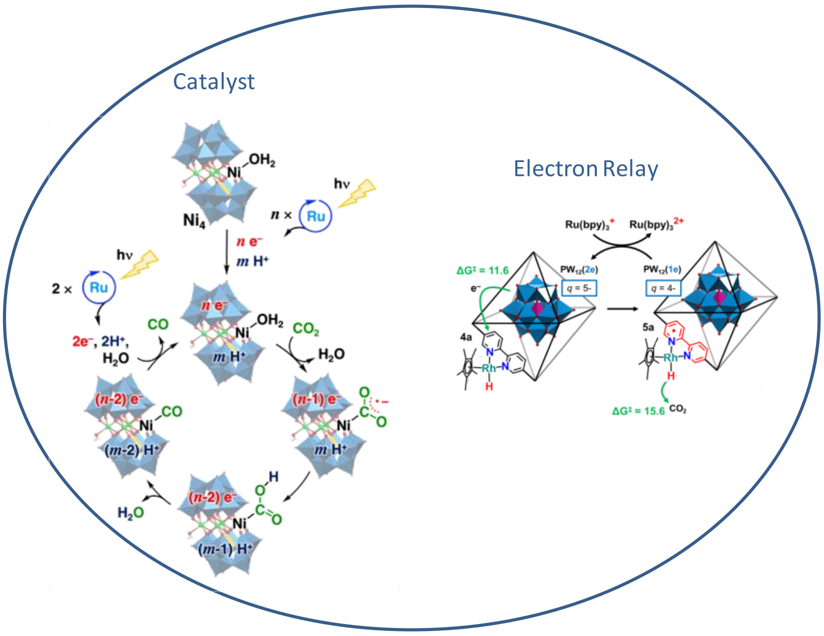
Due to their high tunability, stability and optical and redox properties, polyoxometalates (POMs) can be used in a very wide range of photocatalytic reactions (oxidation of organic substrates, HER (Hydrogen Evolution Reaction), OER (Oxygen Evolution Reaction), CO2RR (CO_2 reduction reaction,…).[1] In this type of process, POMs act as catalysts in the vast majority of cases, but they can also play other roles.

Here, we will first present a classical case where nickel(II) POMs act as homogeneous photocatalysts for the CO2RR.[2] In a second part, we will evidenced that POMs can be efficiently used as co-catalysts, playing the role of electron relay in the heterogenous photocatalytic carbon dioxide reduction reaction.[3]



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Photoelectroactive covalent hybrids based on (iso)porphyrin-polyoxometalate assemblies

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Polyoxometalates (POMs), are promising candidates for various photoelectrochemical applications due to their excellent photosensitivity, redox, and catalytic properties, as well as their relative stability.[1,2] However, POM clusters in their ground state can primarily be excited by UV light, which induces a charge transfer from oxygen atoms to the d^0 transition metal. This limits the application of POMs in solar-driven catalysis.[3] In order to address with this problem, we have designed covalently (iso)porphyrin-polyoxometalate hybrid material [4-5], such as Fe^{III}POM-ZnT2isoP• copolymer by electropolymerization of the 5,15-ditolylporphyrin of Zn (ZnT$_2$P) in the presence of the hybrid POM Py-Fe^{III}POM-Py where the (iso)porphyrin subunit acts as an electron donor and the POM building block serves as an electron acceptor.

This process was monitored using cyclic voltammetry and EQCM (Electrochemical Quartz Crystal Microbalance). Their electrical properties were studied using electrochemical impedance spectroscopy (EIS) and their photovoltaic performances were evaluated through photocurrent transient measurements under visible-NIR light irradiation. The photocurrent for the Fe^{III}POM-ZnT2isoP• copolymer reached up to -600 µA/ cm^2. Finally, the morphology characterization was carried out using Atomic Force Microscope (AFM). However, the application of hybrid materials in the energy conversion domain still requires further investigation.

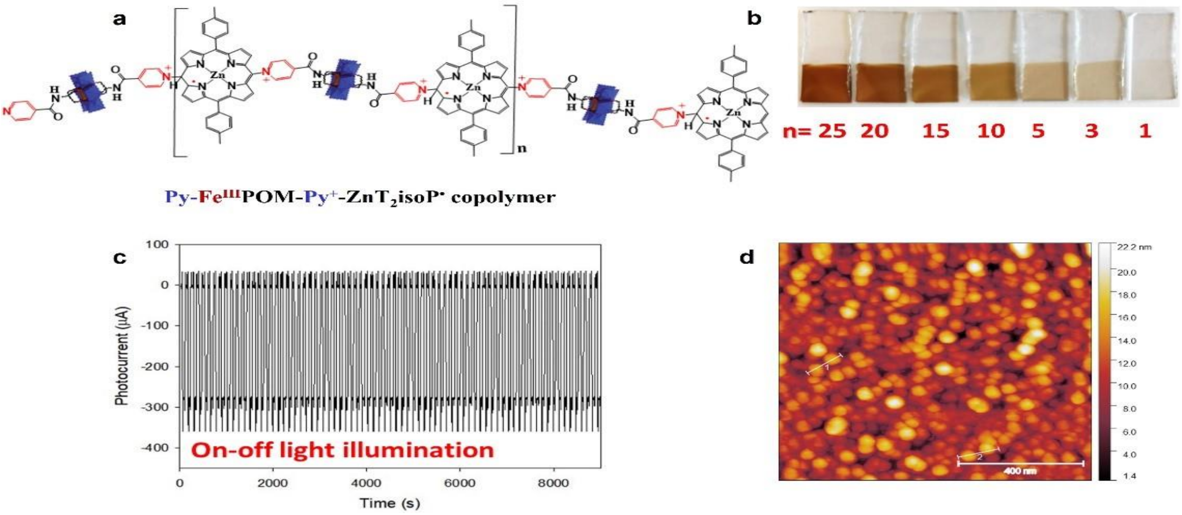

Figure 1. a) Electropolymerization process; b) Fe^{III}POM- ZnT$_2$isoP$^•$ copolymer deposited on ITO with different scan numbers; c) Transient photocurrent test within 4 h; d) Morphology characterization by AFM.

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Photochromism of novel electropolymerized systems that combine diarylethene and porphyrine moieties: studied with using Spectroelectrochemistry and Ultrafast Absorption Spectroscopy

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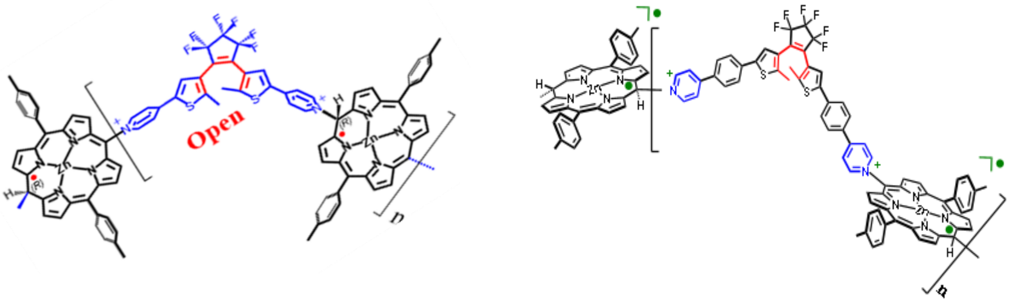
The photochromic behavior of two novel polymers (P1 and P2 see figure below) that combine diarylethene (DAE) and isoporphyrins (IsoP) moieties by electropolymerization have been investigated using spectroelectrochemistry and ultrafast absorption spectroscopy. Preliminary results have shown that the polymers are photochromic in solution but not in solid state. In consequence, this study aims to uncover the ultrafast dynamics behind the distinct photochemical and photophysical behavior of these systems in the different environments. The results reveal two distinct photoinduced processes: in the polymer films, UV excitation induces photoinduced electron transfer (PET) from the isoporphyrin unit to pyridine(Py+), while in solution, PET is followed by photocyclization responsible for the change of color. These findings highlight the critical role of the physical form in controlling photochromic behaviour, providing insights into the state-dependent molecular dynamics.



P 1 = poly-DAE(Py)$_2$-ZnT$_2$isoP•

P 2 = poly-DAE(Ph-Py)$_2$-ZnT$_2$isoP•

Figure: Chemical Structures of electropolymers P1 and P2.

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The Viridium Radical Cations

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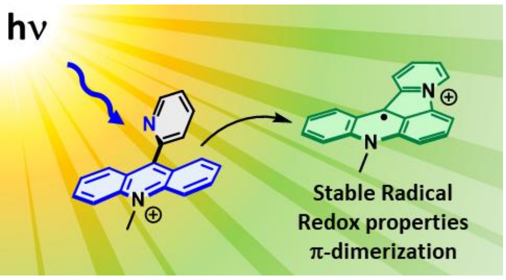
Organic radicals are often discussed as transient and reactive species involved in homo/hetero radical-radical coupling, hydrogen abstraction and disproportionation reactions. Nevertheless, since the discovery of the first persistent organic radical by Gomberg in 1900, thermodynamic stabilization of organic spins was enhanced by extension of the π-system and/or introduction of heteroelements.[1] Original methodologies for the generation of organic radicals has often preceded the emergence of innovative and fertile disciplines. In this context, the acridinium core – a π-extended pyridinium derivative – possesses accessible photophysical properties.[2] On the contrary to the pyridinium core, photochemical derivatization of the acridinium ring is less encountered on account of its extended and therefore more stable π-system.[3]

The discovery of a stable organic radical formed under mild, clean and efficient light-mediated conditions is discussed.[4] The structure of the stable acridinium-based radical photoproduct was unambiguously established by single-crystal X-ray diffraction, mass spectrometry and in solution by EPR, UV/Vis, NMR spectroscopies. The photochemical mechanism of its formation has been elucidated by photophysical experiments coupled to EPR experiments and theoretical investigations. This unique aromatic radical is featured by an amphoteric redox behavior and π-dimerization properties. Its ability to π-dimerize has been demonstrated in water and in the less studied perfluorohexane, two solvents of opposite polarity. By a simple counter-ion exchange, direct comparison of π-dimer thermodynamics between both antagonist solvents allowed an elucidation of the solvophobic behavior in perfluorocarbon.



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Cooperative photoswitching materials

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Cooperativity represents a fascinating phenomenon that brings considerable benefits in terms of time, space and energy control in many domains.[1] Complexation and release of oxygen by haemoglobin to maintain metabolitic homeostasis are typical amplified effects, thanks to highly synergistic conformational and tension changes, triggered by pH modifications. Such amplification has been exploited in nanomedicine to release drugs in a nonlinear way due to strong electrostatic repulsions caused by protonation/deprotonation sequences.[2] Cooperative phenomena are also involved in spin-crossover molecular systems, where abrupt bistability, triggered by an external stimulus, is highly sought for high-speed memories or switches.[3] Whereas cooperative effects have long been studied in polymeric materials,[4] very little attention has been paid on small molecule-based functional materials (SMFMs) whose molecular constitution could nicely be harnessed to lead to extensive structural rearrangements under tiny perturbations. This, however, requires high control of the mutual interactions to impulse large actuation that can be transduced at the macroscopic level.

Thanks to the use of glass-forming SMFMs, we show that extensive deformation, photoinduced by light, highly depends on the mutual intermolecular interactions between the individual molecules and can be modulated by varying the ratio of H-bonding entities.[5] Such cooperative effects have been extended to self-assembled photochromic nanoparticles manufactured by flash precipitation.[6] Geometry photoswitching can reversibly be triggered in solution and followed at the single nanoparticle level by combining atomic force microcopy (AFM) and *in situ* dual illumination. Progressive disintegration of the nanoparticles after several cycles of expansion-contraction caused by alternating vis and UV illuminations could be observed and ascribed to strong adhesion effects (Figure 1).[7] The latter results open perspectives into the design of drug-delivery nanocarriers where on-command drug release should better exploit the strong non-covalent intermolecular interactions established at the interface between nanoparticles and biological tissues.

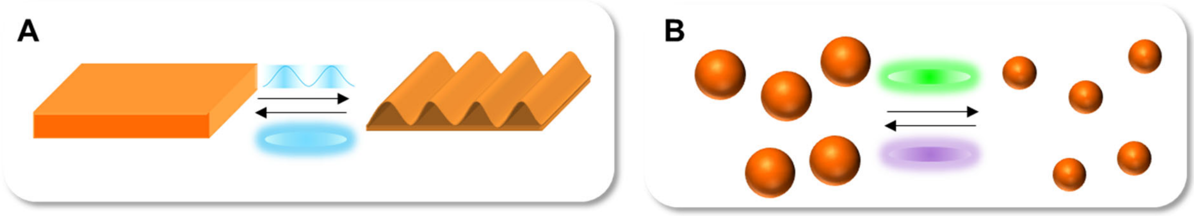

Figure 1. A) Sub-micrometer-high reliefs of thin films under structured illumination. B) Photoswitching of nanoparticles under dual color excitation.

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Amplified switching by cascade reaction in photochromic terarylenes

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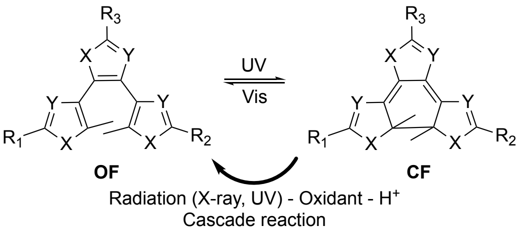
Photochromic compounds undergo a light-induced reversible reaction, between two species, and are widely known for their color changing ability. Among them, terarylenes, a sub-family of diarylethenes, shuttle between an open form (**OF**) and a closed form (**CF**) [1,2]. The latter is significantly stable (several days to years). Also, switching of terarylenes can be triggered by other means than light (e.g. X-ray, oxidant, acid), involving redox or acid-base reactions (Scheme 1) [3-7]. Moreover, in some cases, a cascade reaction takes place, where one single trigger occurrence leads to the switching of several molecules [4,5].



Scheme 1. Switching of terarylenes (for example X = S, Y = N)

Examples of such processes will be introduced in this presentation.

- In one of them, UV radiation activates a redox reaction-based cascade **CF** to **OF** reaction [8]. In addition, to provide more visible color change, Nile Red was added to microcapsules containing tearylenes, and its fluorescence switched.
- In another one, the addition of acid to a solution containing **CF** speeds up the back reaction to **OF** by a factor of 1500, owing to the lower stability of **CF-H**$^+$, the protonated form of **CF** [9]. Moreover, a sub-stoichiometric amount of acid is enough for a total transformation of **CF** to **OF**. Neutralization of the acid by a base allows to perform further cycles of switching.

Both fundamental mechanistic aspects and application-oriented perspectives will be discussed. Indeed, such trigger and subsequent cascade processes are promising, for example, to design sensitive dosimeters, or in molecular solar energy thermal (MOST) storage and release systems.

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Easy processable photomechanical thin film involving a photochromic diarylethene and a thermoplastic elastomer in supramolecular interaction

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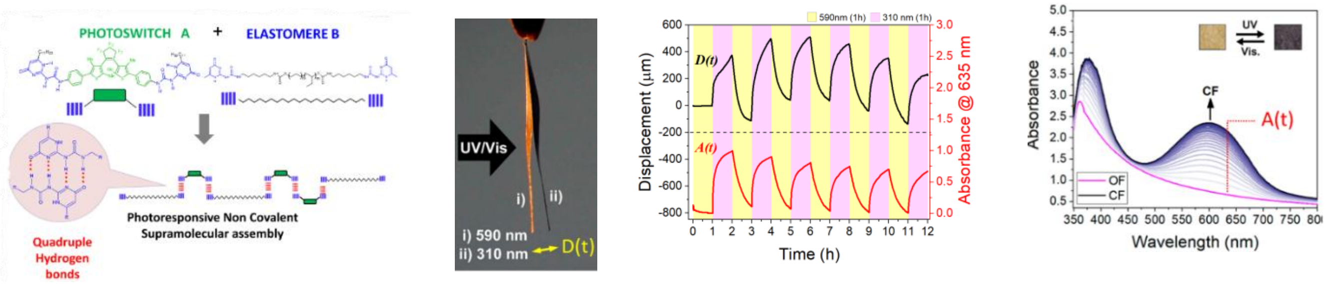
As an alternative to liquid crystal elastomers (LCE) involving azobenzene (AZO) units or photochromic microcrystals, a novel supramolecular photoactuator is presented in the shape of a thin film of centimetric size. The thin film is easily obtained by spin coating and does not require any alignment or crosslinking. Chemically, this photoactuator combines a photochromic dithienylethene (A) functionalized with ureidopyrimidinone (UPy) units with a telechelic thermoplastic elastomer (B) also functionalized with UPy units, which allow for connections between the two compounds via quadruple hydrogen bonds. Upon alternating UV/visible light irradiation, a reversible bending/flattening movement was observed together with a reversible change of color. Both processes were studied using a displacement and absorption tracking setup respectively. For the first time, the PME is quantitatively correlated with the photochromism evidencing that the DTE units induce the movement in the same way for UV (photocyclization) and Visible (photoreversion) light excitation. Then, based on various material science technics implementing in-situ illumination, the PME is explained in terms of photoinduced strain generated inside 160 nm UPy-bonded dithienylethene domains that reversibly expand and contract (by about 50%) under UV and visible light, respectively. The semi-crystallinity of the elastomer and a strong supramolecular network connecting both A and B have been identified as important parameters to efficiently turn the microscopic photo-strain into macroscopic actuation.



a) b) c) d)

Figure 1 a) DTE (A) and semi-crystalline elastomer (B) both functionalized with UPy units; b) snapshot of photoactuator (cutted stripe of thin film) in motion upon UV and Visible irradiation respectively; c) Real time Displacement of the tip of the photoactuator (black curve) and absorbance change (red curve) for 6 irradiation cycles (UV/Vis 1 hour each); d) Absorbance of the thin film and selected wavelength for the absorbance tracking.

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