



GDR CNRS
Photoelectrostimulation
27-28 November 2023
Nantes University

Booklet of Abstracts

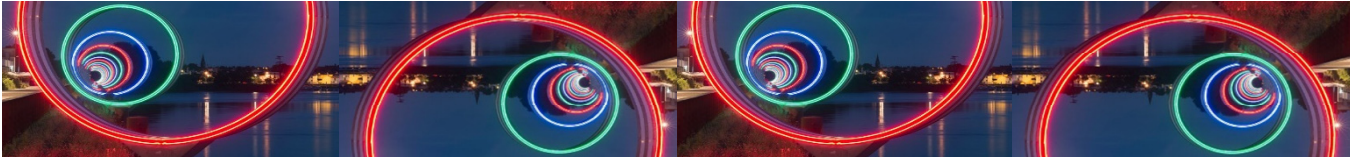
Programme Journées Plénières RT CNRS Photoélectrostimulation 2
Nantes Université – LS2N (bâtiment 34)
27-28 novembre 2023

Monday 27 November 2023

	13h	WELCOME COFFEE		
	13h45-14h	OPENING ADDRESS		
Session 1	14h-14h40	PL01	Laurent RUHLMANN	Photo(redox)-active and photo(electro)switchable materials: a journey from molecular design to applications
	14h40-15h	C01	Ludmilla VERRIEUX	Vibronic coupling investigation to study the photophysical properties of azabodipy compounds
	15h-15h20	C02	Ali DABBOUS	Plasmon-driven photoelectrochemistry in tetrazine derivatives at the microscopic scale
	15h20-15h40	C03	Yoann FREROUX	New boranil-based antennae for photoswitchable luminescent lanthanide (III) complexes
	15h40-16h10	COFFEE BREAK – POSTER SESSION		
	16h10-16h30	C04	Thomas COTTINEAU	Electrosynthesis of TiO ₂ nanotubes electrodes with variable thickness and localized rapid analysis of their photoelectrochemical properties
Session 2	16h30-16h50	C05	Elie BOU RAHHAL	Formation of controlled TEMPO-based layers: From the elaboration to the electrocatalysis application
	16h50-17h10	C06	Baptiste MAILLOT	Surface optical nanometrology: mechanism and control of diazonium derivatives photografting
	17h10-17h30	C07	Guillaume IZZET	Tuning photoinduced electron transfer in photosensitized polyoxometalate-based hybrids
	17h30-17h50	C08	Rana MHANNA	Geometry-driven mass transport dynamics within permeable 3d-microstructures fabricated by two-photon polymerization with γ -shaped triphenylamines initiators
	18h-19h30	COCKTAIL – POSTER SESSION		
	20h	DINNER – LA PRISON DU BOUFFAY (BOUFFAY SQUARE, NANTES)		

Tuesday 28 November 2023

8h30		WELCOME COFFEE		
Session 3	9h-9h40	PL02	François RIOBÉ	The mischievous properties of Ln(III) complexes: switching the luminescence for unexpected reasons
	9h40-10h	C09	Chloé BILLIAUX	Polyoxometalate-based hybrid materials: Toward the stabilisation of optically active benzazolo-oxazolidine derivatives in the solid state.
	10h-10h20	C10	Antonio RIQUELME	Insights from optoelectronic small perturbation techniques on photovoltaic process in photochromic dye-sensitized solar cells
10h20-10h50		COFFEE BREAK – POSTER SESSION		
Session 4	10h50-11h10	C11	Pierre-Antoine BOUIT	Tetrazo[1,2-b]indazoles: new scaffold for photoelectrostimulation?
	11h10-11h30	C12	Stephania ABDALLAH	Two-photon active o-carborane branched initiators for 3d microfabrication of thermo-switchable fluorescent materials devoted to optical data storage
	11h30-11h50	C13	Federico ZIZZI	Photocrosslinked azo nanoparticles as potential photoacoustic imaging markers
	11h50-12h10	C14	Isabelle LERAY	Synthèse et études photophysiques de sondes fluorescentes greffées sur cellulose
12h10-14h		LUNCH – POSTER SESSION		
Session 5	14h-14h20	C15	Laurent BOUFFIER	Circularly-polarized electrochemiluminescence
	14h20-14h40	C16	Leyli IBRAHIMLI	Stabilizing and enhancing the properties of copper(I) photosensitive complexes by entrapment in silica nanoparticles
	14h40-15h	C17	Olivier GALANGAU	Redefining the trade-off relationship between h-bonds and dispersive interactions in cooperative supramolecular polymerization
	15h-15h20	C18	Syamasrit DASH	Hexaphyrin-cyclodextrin hybrids: redox switching between Möbius and Hückel aromatic systems in chiral environment
	15h20-15h40	C19	Olivier BURIEZ	Electrochemiluminescence imaging of the permeabilization of single giant liposomes
15h40-16h		ORAL COMMUNICATION PRIZES – CLOSING ADDRESS		



Booklet of Abstracts

Plenary Lectures

Photo(redox)-active and photo(electro)switchable materials: a journey from molecular design to applications

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The conference will be divided into two parts. The first part will be on the development of hybrid systems incorporating polyoxometalates (POMs) which is a promising approach to elaborate new redox active materials. To expand the practical applications, their association to a visible-light photosensitizer is needed and has been explored (Fig. 1). In this context, we have also developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin radical cation or dications. The formation of hybrid POM-porphyrin copolymeric films (Fig.

1b) can be obtained by the electro-oxidation of porphyrin in the presence of the hybrid POM bearing two pyridyl groups (Py-POM-Py).^[1-2] Using the same methodology, the synthesis of a diarylethene-(iso)porphyrin photoswitchable copolymer has been developed (Fig. 1c). The incorporated diarylethene maintains its reversible photochromism upon the UV-Vis radiation with multiple cycles of ring-opening and closing.^[3] A photo-switchable molecular capsule based on Keggin-type POM and diarylethene has been also formed and studied (Fig. 1a).^[4] In the second part, the photoredox-switchable molecular grippers based on resorcin[4]arene cavitand platforms equipped with alternating quinone (Q) and quinoxaline walls carrying hydrogen bond donating groups will be presented. The semiquinones (SQ) state can be generated electrochemically and photochemically.^[5] It was shown that these systems adopt

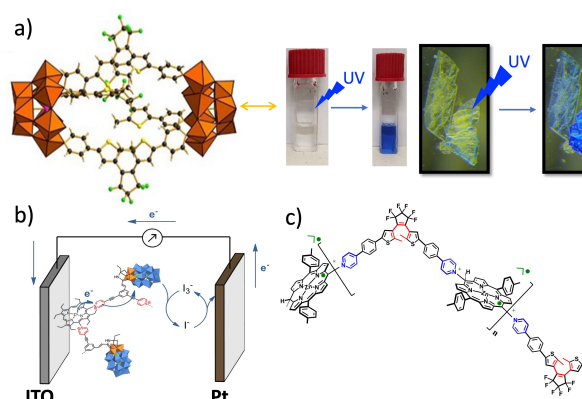


Fig. 1 Various type of photo(redox)-active or photo(electro)switchable systems studied.

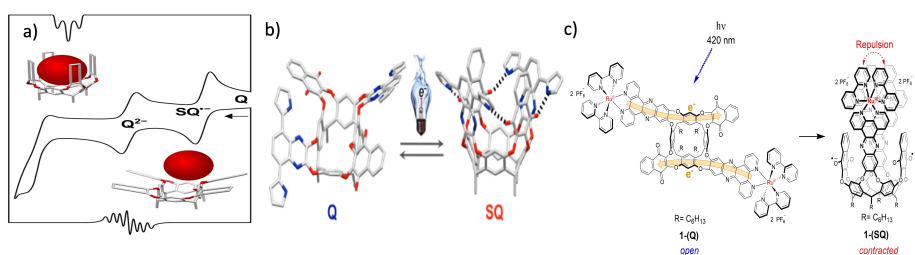


Fig. 2 Photoredox-switchable molecular grippers based on resorcin[4]arene cavitand platforms.

an open conformation in the oxidized Q state until redox interconversion to the paramagnetic SQ radical anion provides the stabilization of the closed form through hydrogen bonding.

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The mischievous properties of Ln(III) complexes: switching the luminescence for unexpected reasons

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Previous works of our team were dedicated to the design and the study of lanthanide complexes with high-brightness due to the sensitization by tailor-made charge-transfer antennas, enabling tridimensional functional imaging through two-photon excitation.^[1] More recently, we used this expertise in the ongoing effort to harness the unmatched Circularly Polarized Luminescence (CPL) properties of chiral lanthanide emitters, thanks to the development of state-of-the-art fast-CPL apparatus.^[2]

Through these years, we have learned, sometimes the hard way, that changes in the emission of a Ln complex should not always be viewed solely through the lens of the molecular chemist, seeking a direct structure-property relationship. Indeed, essential principles of photophysics or simple optical artefacts may be overlooked and can sometimes explain some intriguing phenomena. This will be illustrated with a few recent instances we encounter over the past years.

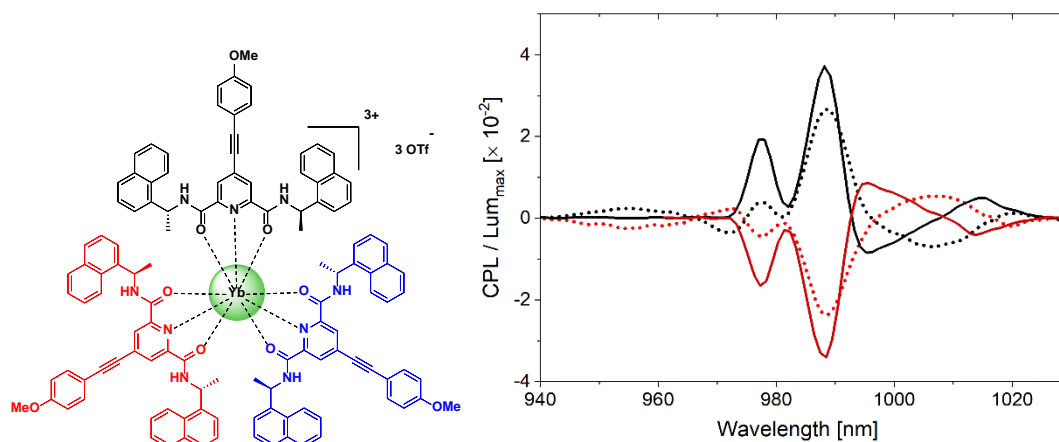


Figure: structure of a chiral Yb-complex and related CPL measured at 300 K (solid line) and 4 K (dotted line) on both enantiomers.

References

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Booklet of Abstracts

Oral Communications

Vibronic coupling investigation to study the photophysical properties of azaBODIPY compounds

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AzaBODIPY (Figure 1.A) are a class of fluorophore which have experienced exponential growth in wide range of applications and are today promising candidates for medical imaging and fluorescence guided surgery. ^[1] In this context their experimental development is based on optimizing the nature of the ligands and replacing the boron center with another metal atom (aza-M-DIPY, M = metal), ^[2] in order to shift the absorption and emission wavelengths further in the NIR region, and increase their fluorescence quantum yield. To establish such structure-properties relationships, their vertical photophysical properties can be accurately computed with TD-DFT. Taking into account vibrational contribution and non-radiative mechanisms is necessary to achieve a more correct description of the photophysical properties. ^[3] In this contribution we show how the use of TD-DFT coupled with vibronic models ^[4] can help rationalizing the spectra band structure (Figure 1) and guide the design of more efficient aza-M-DIPY emitters by computing their fluorescence quantum yield.

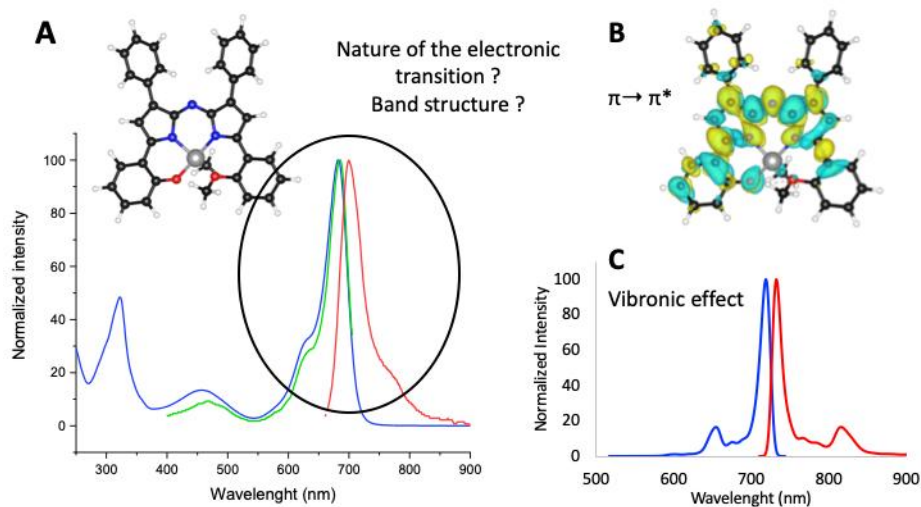


Figure 1.A. Experimental absorption (blue) and emission (red) spectra of an aza-Al-DIPY compound. The green curve is excitation. **B.** Density difference between ground and excited states for absorption of the aza-Al-DIPY compound. Yellow and blue surfaces represent gain and loss of electronic density, respectively. **C.** Computed spectra obtained by vibronic model.

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Plasmon-driven photoelectrochemistry in tetrazine derivatives at the microscopic scale.

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The use of plasmonic nanoparticles (PNP) for energy conversion applications is an object of an intense research effort. PNPs possess specific optical and physical properties, providing the ability to support localized surface plasmon resonances (LSPR) and the generation of hot charge carriers in response to convenient excitation. Due to these properties, PNPs attracted significant attention in various fields, including sensing, imaging, photothermal therapy, photocatalysis, and energy storage applications.^{[1][2]}

In this work, plasmonic substrates made of gold nanoparticles (AuNPs) and Tetrazine derivatives as redox-active luminescent probes are selected to study the plasmonic-induced photoelectrochemical processes. A set-up (Fig.1-A) consisting of a focalized laser irradiation and fluorescence microscope combined with scanning electrochemical microscopy (SECM)^[3] was employed to investigate the plasmonic effects.

Two tetrazine derivatives (Fig.1-D) are used to investigate the redox processes either in solution^[3] or on the surface of the AuNPs through grafted monolayer^[4]. In both cases, we show the efficiency of the hot carriers to induce redox reactions with the tetrazine probes. Upon plasmonic excitation, a change in the electrochemical tip current is observed in the SECM measurements, accompanied by the quenching of the tetrazine's fluorescence (Fig. 1-B&C). The variation of the experimental parameters, such as the change of the applied tip potential, the irradiation laser power, and the alignment of the focalized laser with the SECM-UME Tip, as well as the mechanistic investigations of the transferred show that the plasmonic activity is the dominant process in our systems.

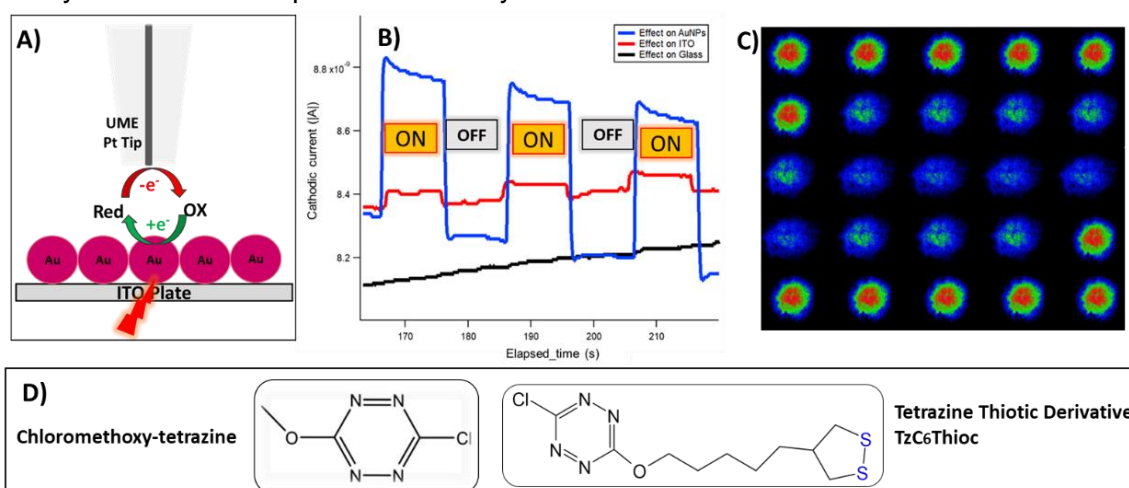


Figure 1: Experimental Investigations: A) Schematic representation of the SECM measurements on the AuNPs-ITO surface. B) The current response monitored during the laser switch ON/OFF. C) Fluorescence quenching of the tetrazine molecules recorded using the fluorescence microscope. D) Molecular schemes of the used Tetrazine derivatives.

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New boranil-based antennae for photoswitchable luminescent lanthanide (III) complexes

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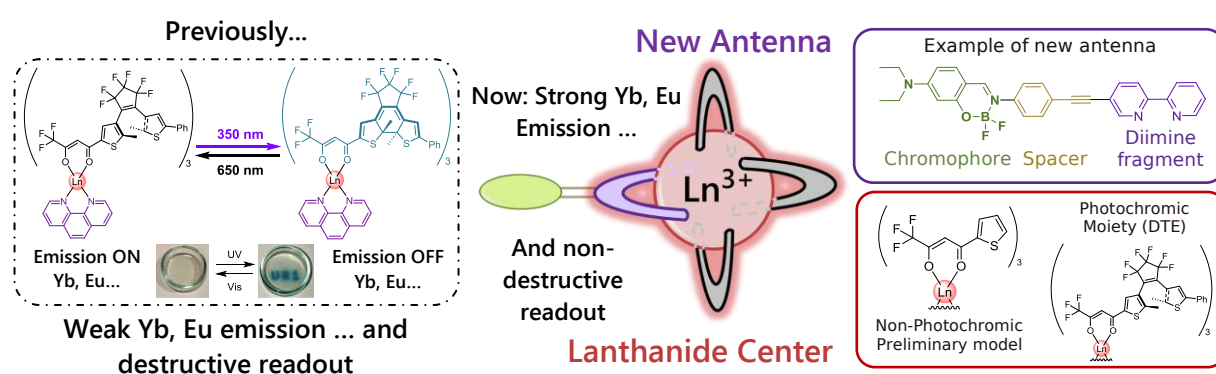
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Counterfeiting is a global problem that challenges businesses, governments, and consumers. In order to develop novel anti-counterfeiting systems, it is particularly interesting to elaborate lanthanide-based complexes due to their original emission features such as long lived and narrow bandwidth luminescence from the visible up to the near infrared spectral range with high emission efficiency.^[1]

Our group recently made a major breakthrough in this field by designing lanthanide complexes which luminescence can be turned on or off at will, with the use of an external photostimulation introduced with a dithienylethene (DTE) moiety. However, this system achieving a multi-level anti-counterfeiting system, suffers from a moderate brightness.^[2a-b]

Our goal is now to design new switchable complexes with a significant brightness improvement and a high on/off ratio to meet the standards required for applications. Here we show the synthesis of new boranil-based chromophore including bipyridine or phenanthroline with high molar absorption coefficient ($> 50\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$) designed to enhance light absorption and provide a brighter luminescence of the lanthanide ions.^[3] The photophysical results shine light on these chromophore abilities to sensitize lanthanide emission in the red (Ln = Eu) and NIR (Ln = Yb) ranges.



References

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Electrosynthesis of TiO₂ nanotubes electrodes with variable thickness and localized rapid analysis of their photoelectrochemical properties

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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 structure 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]

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 TiO₂ nanotubes (NTs) with length increasing gradually from 0 to 15 μm, on a single electrode.^[3] This method was employed

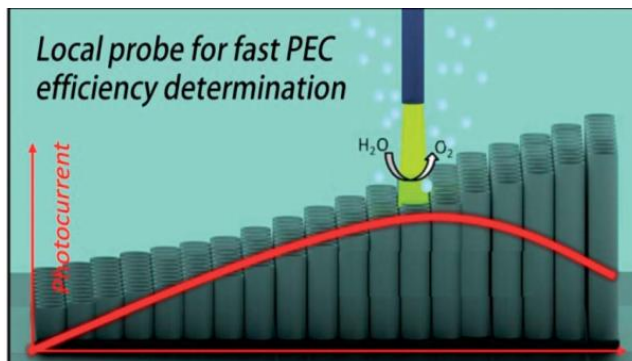


Figure 1: principle of the local probe PEC measurement on variable NTs length electrode.

to synthesize TiO₂-NTs with variable length but also doped TiO₂-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 after simple modeling.

References

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FORMATION OF CONTROLLED TEMPO-BASED LAYERS: From the elaboration to the electrocatalysis application

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The electrocatalytic property of TEMPO group was previously exploited, implying its oxidized version when electro-stimulated on a conductive surface. The enhancement of the electrocatalytic activity in the confined state has required an adaptation of surface properties in terms of accessibility, underscoring the importance of surface dilution [1] and thickness control [2] of the attached organic film. Herein, we propose a novel strategic surface engineering that satisfies the required criteria, by striking at once interfacial reactivity and film stability. Inspired by previous approaches (*i.e.* *Self-assembled monolayers-SAMs & Diazonium salts chemistry*), a molecular strategy is implemented to design organic entities comprising an aryldiazonium cation, a spacer, and a redox group. The choice of diazonium salts as candidates for this methodology refers to their strong/covalent attachment to the surface after being reduced into aryl radicals.

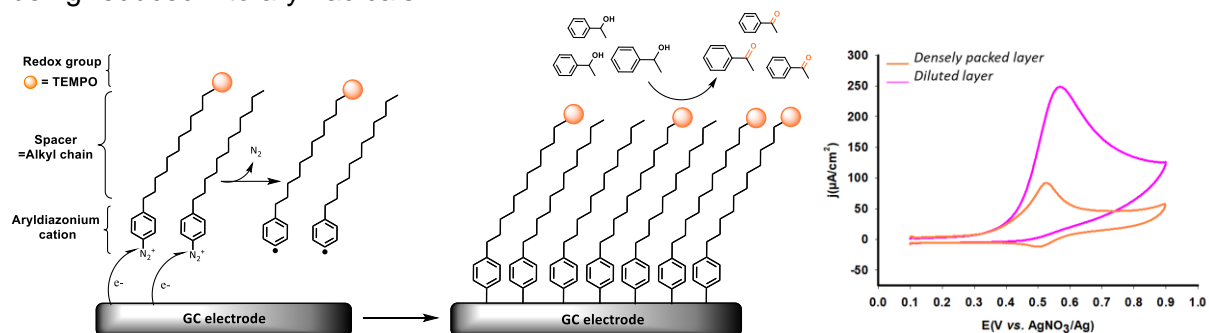


Fig. 1: Elaboration of TEMPO-mixed layer by co-reduction of diazonium mixture, and its electrocatalytic response.

A functionalized molecule and a surface-diluent one are conceived according to the proposed template, to form TEMPO-diluted layers by co-reduction of the corresponding diazonium salts. The use of a long alkyl chain as a spacer allows facing the constraints related to the formation of such mixed layers, by providing a limitation of layer growth [3], and a surface composition control. Subsequently, we can consider modulating the dilution ratio of active species and follow the electrocatalytic performance of different TEMPO-diluted layers. Electrochemical and gravimetric studies of the resulting modified surfaces have shown the suitability of the investigated strategy in the preparation of sustainable and efficient electrocatalytic platforms.

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Surface optical nanometrology : mechanism and control of diazonium derivatives photografting

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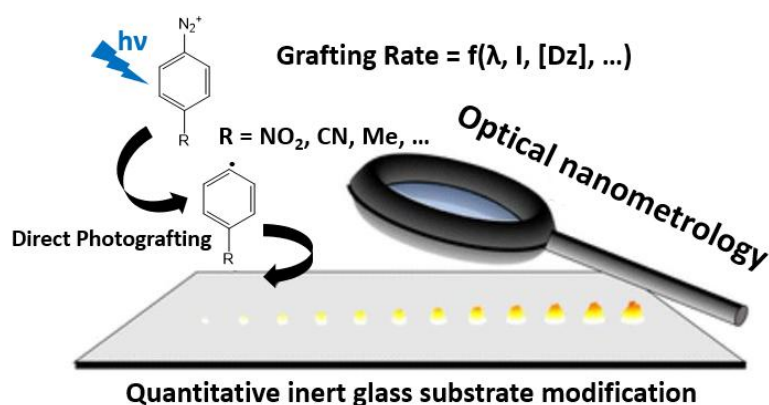
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High resolution and quantitative surface modification through photografting is a highly desirable strategy towards the preparation of smart surfaces with precursors economy. Photografting enables chemical functions to be precisely located onto well-defined regions of surfaces, microstructuring it with sub-micrometric resolution. Quantitative design (i.e. controlling the number of surface grafted groups) requires fine knowledge about surface reaction kinetics, which in turn require extensive calibration of dosing/grafting relationships.

Diazonium salts are popular precursors of versatile aryl radicals, but the mechanisms leading to their direct photoactivation using visible wavelengths [1] are still poorly understood. Indeed, modification of grafting conditions or substituents in the aryl group deeply impact several aspects of the grafting process (concentration, photophysical properties, grafting efficiency). Instead of relying on tedious calibration procedures, which must be redone for any change in the grafting conditions, we hypothesize that quantitative and non-invasive operando monitoring of the surface kinetics would be a major asset for precise surface modification.

Quantitative phase imaging is a nanometrology tool for evaluating the local grafting rate with diffraction-limited resolution and nanometric precision. By measuring the surface modification kinetics under a range of different conditions, the influence of key parameters on the reaction mechanism can be readily evaluated, such as the laser power density, the radical precursor concentration and the presence of side reactions [2]. In this communication we will show that this technique can be used to gather quantitative information about the grafting process, which in turn can be used to control the surface reaction. We show that general and precise control strategies can be designed using relatively simple instrumentation to control the volume of the grafting material with 5% precision, in spite of widely different surface grafting kinetics spanning four orders of magnitude [3].



References :

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[3] Maillot, B.; Audibert, J. F.; Miomandre, F.; Brasiliense, V. Nanometrology based control: Taming uncontrolled aqueous radical grafting and polymerization reactions (in preparation)

Tuning photoinduced electron transfer in polyoxometalate-based hybrids

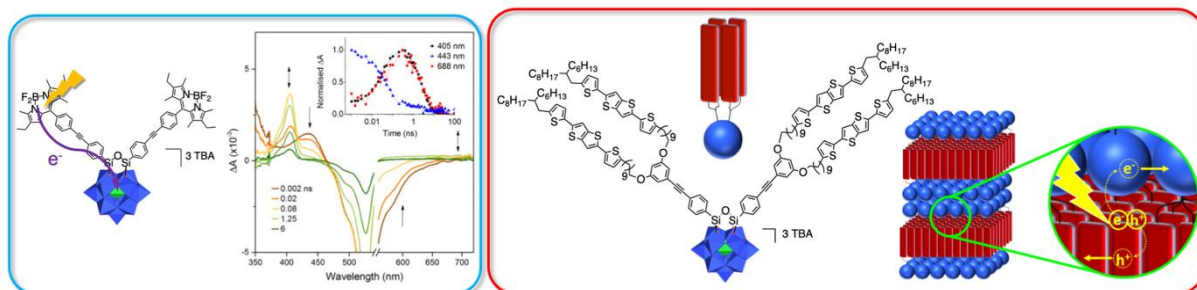
Kevin Mall Haidaraly,¹ Fabrice Mathevet,¹ Christian Cariño,¹ Anna Proust,²
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Polyoxometalates (POMs) form a remarkable class of well-defined nanosized oxoclusters with an unmatched diversity of structures and properties. An important feature of POMs is their ability to reversibly accept and release specific numbers of electrons under minor structural rearrangement. Therefore, POMs are attractive candidates for the development of photochemical devices aiming at photocumulative electron transfer. In this context, we developed hybrid compounds in which chromophores are covalently connected to a POM and stimulate electron transfer to the oxocluster upon excitation.[1] In these systems, the occurrence of photoinduced electron-transfer and the lifetime of the resulting charge separated state are not only dependent of the redox properties of both components but also by the chemical environment around the POM unit.

This will be presented along with our last results obtained with a family of POM-bodipy dyads and a photoactive POM-based mesogenic hybrid.[2] We will describe the synthetic strategy and photophysical properties of this modular system as well as the development of preliminary photonic devices.



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Geometry-driven Mass Transport Dynamics within C08 Permeable 3D-Microstructures fabricated by Two-Photon Polymerization with Y-shaped Triphenylamines initiators.

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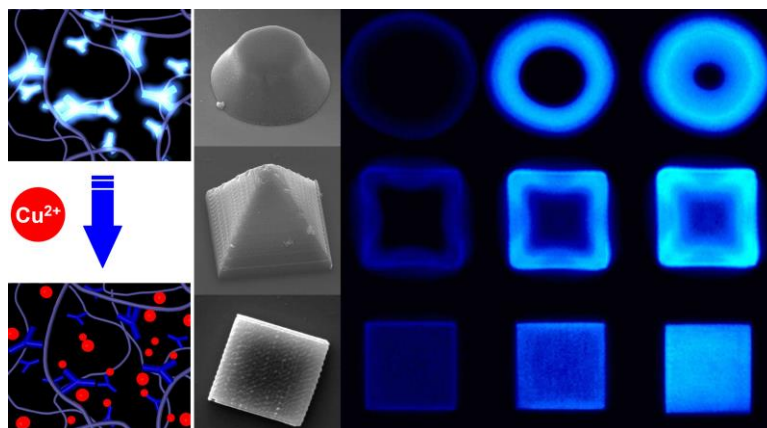
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Two-photon stereolithography (TPS) is a layer-by-layer assembly technique that has proved to be a powerful tool for the fabrication of intricate 3D microstructures with very high spatial resolution¹. Due to TPS numerous and versatile applications, the conception of two-photon active materials according to the established structure-property relationships²⁻³ has gained great interest recently.

In line with these structure-property relationships, we have elaborated a series of multi-branched triphenylamines photoinitiators⁴

which incorporate an electron donor group (triphenylamine) decorated with electron acceptor group (ketone) and with substituents such as anisole and thioanisole. We describe herein the one-photon and two-photon photophysical properties of these



chromophores, their photopolymerization efficiency as well as their applications, in particular in two-photon stereolithography. Of particular interest, we demonstrate a luminescence ON-OFF process controlled by quenching diffusion dynamics which can be modulated by the geometry and topology of the permeable 3D microstructures.

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Polyoxometalate-based hybrid materials: Toward the stabilisation of optically active benzazolo-oxazolidine derivatives in the solid state.

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The benzazolo-oxazolidine (BOX) derivatives represent an interesting family of multiswitchable molecules. They can respond in solution to different kinds of stimulation such as electrochemical potential, pH variation or light irradiation^[1] leading to the generation of a cationic species coming with a strong modulation of their optical characteristics. In order to efficiently transpose their properties into the solid state and to design new optically active materials, the coupling of BOXs with polyoxometalates^[2] (POMs: anionic metal-oxide clusters) into new organic-inorganic supramolecular materials is a promising but still unexplored approach.

In such context, we report here our success designing crystallised supramolecular assemblies combining POM and BOX units. They are exhibiting a large versatility in their synthesis pathways, chemical compositions and crystal structures. Among them, materials using MeBOX(Ph-NMe₂) or MeBOXacridine as BOX derivative, are demonstrating the capacity of the [M₆O₁₉]²⁻ (M= Mo, W) to stabilise different cationic forms of these BOXs under acid stimulation (Fig.1). Thereby, the hybrid material (MeBOX(Ph-NMe₂))₂[M₆O₁₉] (M= Mo, W) exhibits efficient reversible halochromic properties upon acid vapours exposure at room temperature characterised by a colour change. This effect is due to the capture of HCl into the hybrid networks stabilising the Open Protonated form of the BOX^[3]. Surprisingly, using the tungsten derivative leads to a photoluminescence modulation upon acid exposure. By using different crystallisation technics and various type of stimulation for the BOX, it was possible to obtain different hybrid assemblies including the different protonation states of the BOX ((MeBOXacridine)₂[M₆O₁₉] and (MeBOXacridinium)₂[M₆O₁₉].2Cl-) (Figure 1). Strikingly, the MeBOXacridinium.Cl- is showing photoluminescence in the solid state as a purely organic unit. The loss of this property inside the hybrid material is showing the propensity of this unit to form charge transfer with POM moiety.

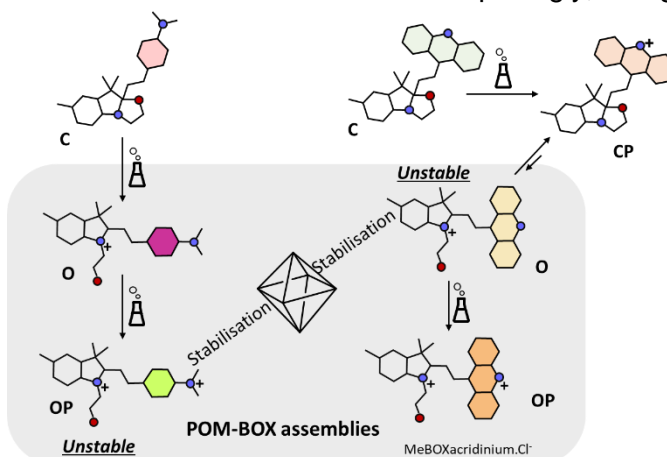


Figure 1 : Different protonation states of the MeBOX(Ph-NMe₂) and MeBOXacridine and POM stabilisation

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Insights from Optoelectronic Small Perturbation Techniques on Photovoltaic Process in Photochromic Dye-Sensitized Solar Cells

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The development of photochromic dye-sensitized solar cells (DSSCs), which can self-adapt their light transmission to the intensity of the ambient light, could be crucial for developing Building Integrated Photovoltaics (BIPV). We focus on the previously reported diphenyl-naphthopyran series,¹ analyzing their optoelectronic behavior by adapting small-perturbation techniques to the inherent properties of the photochromic dye to unravel the electronic processes at the electrode-dye-electrolyte interfaces². We molecular engineering to develop different series of naphthopyran dyes with an identical pi-conjugated backbone and varying alkyl substituents reported to control the discoloration kinetics and reduce the recombination processes, achieving power conversion efficiencies of over 4.3%³. Finally, a co-sensitization approach combining photochromic dyes was explored to improve the optical properties of the device.



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Tetrazo[1,2-*b*]indazoles: new scaffold for photoelectrostimulation?

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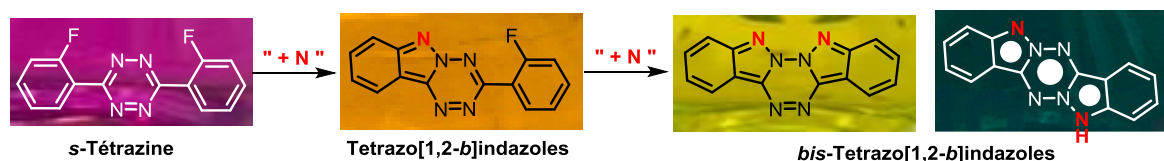
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The straightforward access to a new class of aza-polyaromatics will be presented. Starting from readily available fluorinated *s*-tetrazine,[1] a cyclization process with azide[2] leads to the formation of an unprecedented tetrazo[1,2-*b*]indazole or a bis-tetrazo[1,2-*b*]indazole (cis and trans) (see scheme).[3] Based on the new nitrogen core, N-directed metal-catalyzed ortho-C–H bond functionalization allows the easy functionalization of the novel platform. The physicochemical properties of these compounds were studied by a joint experimental/theoretical approach. The tetrazo[1,2-*b*]indazoles display solid-state π -stacking, low reduction potential, absorption in the visible range up to the near-infrared (NIR) and intense fluorescence, depending on the molecular structure.

Implementation of this cyclization method to other N-rich heteroaromatics as well as taking advantage of the specific N-reactivity can lead to the development of novel NIR dyes, open-shell polyaromatics as well as incorporation into optoelectronic devices.



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Two-Photon Active *o*-Carborane Branched Initiators for 3D Microfabrication of Thermo-Switchable Fluorescent Materials devoted to Optical Data Storage

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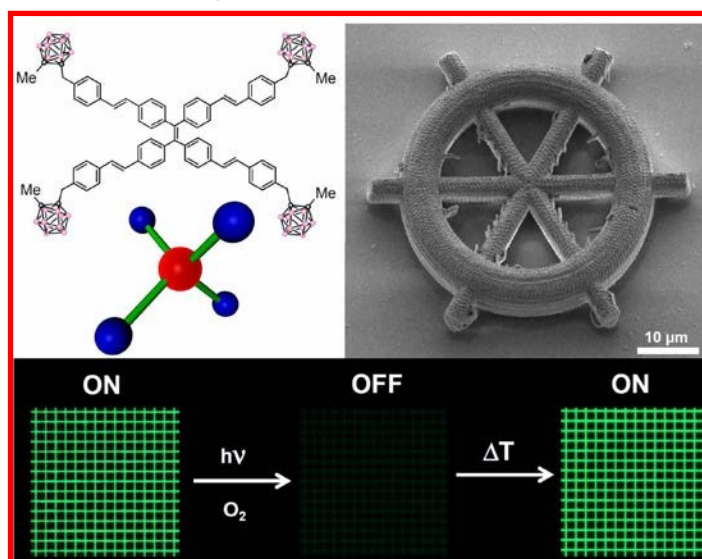
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Keywords: Two-Photon Absorption, 3D-Stereolithography, Stimuli Responsive Photomaterials

Two-photon polymerization (2PP) has emerged as one of the most efficient maskless stereolithography[1]. Such a direct laser writing method allows the fabrication of intricate 3D-structures with a spatial resolution down to the sub- μm scale. The unique capability of 2PP relies on its diffraction unlimited spatial confinement due to the non-linear absorption of the initiator component which is photoactivated at the focus point of a tightly focalized *fs*-pulse laser[2]. 2PP technology which is now commercially available has been largely dedicated to the photopatterning of advanced functional materials with plethora applications such as photonic metamaterials[3], stimuli responsive devices[4], microelectromechanical systems or micromedicine[5, 6]. In this context, the two-photon initiator clearly has a pivotal role and should both exhibit significant two-photon absorption (2PA) cross-sections as well as an efficient quantum yield for the generation of reactive species that promote monomers cross-linking. With this respect, we present herein a series of *o*-carborane-based derivatives with quadrupolar or octupolar geometries with significant two-photon activation ability. Such a non linear absorption property has been oriented for 2PP fabrications of emissive microstructures whose fluorescent can be alternatively 'switched off' and 'switched on' through light and thermal stimuli. This strategy proposes thereby a two-photon patternable materials for reversible data storage applications.



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Photocrosslinked azo nanoparticles as potential photoacoustic imaging markers

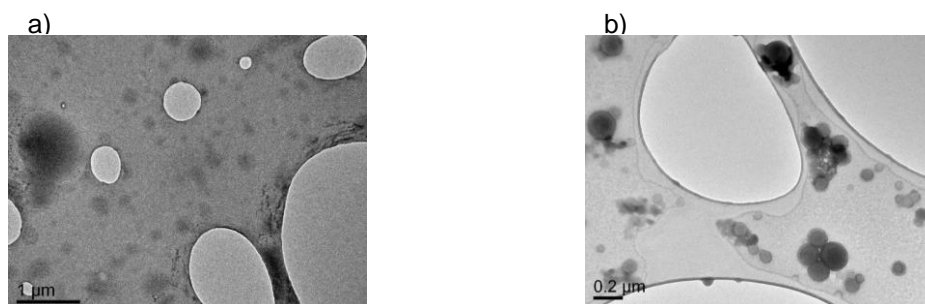
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Photoacoustic imaging (PA) is an emerging and non-invasive technique that exploits the known “photoacoustic effect”, based on the generation of acoustic waves after light excitation of chromophores.^[1] Although biological events can be dynamically followed up, high concentration of absorbing molecules is required. To overcome this limit, organic nanoparticles, comprising a high payload of dyes, have appeared as a promising alternative to molecular dyes in solution. Thus, we prompted our interest in azo photochromic compounds characterized by high photostability, significant geometry and vibrational motions in the excited state, to allow for enhanced PA imaging contrast. Azo NPs will also imply crosslinked architectures, to avoid their disassembling since they are issued from mere flash precipitation of dyes in water. With this aim, thiol(dithiolane)-ene photopolymerization, compatible with aqueous conditions, has been privileged^[2,3] and involved crosslinkers with varying flexibility to modulate the mechanical properties of the final nanostructures, and their resulting photoacoustic signal. TEM analyses revealed notable differences in geometry between pristine and photocrosslinked NPs, the latter displaying a well-defined spherical



shape.

Figure 1. TEM imaging of azo nanoparticles deposited on a carbon-coated grid. a) Before photocrosslinking; b) After photocrosslinking.

The ability of azo NPs to modulate their geometry upon E-Z photoisomerization has been validated by absorption spectroscopy revealing reversible evolution of the absorbance. As a prospect, AFM measurements under light illumination will be carried out to characterize the photoinduced change in geometry of azo NPs, while photoacoustic investigations need to be performed as a function of light to assess the impact of the photoreaction on the generation of acoustic waves.

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Synthèse et études photophysiques de sondes fluorescentes greffées sur cellulose

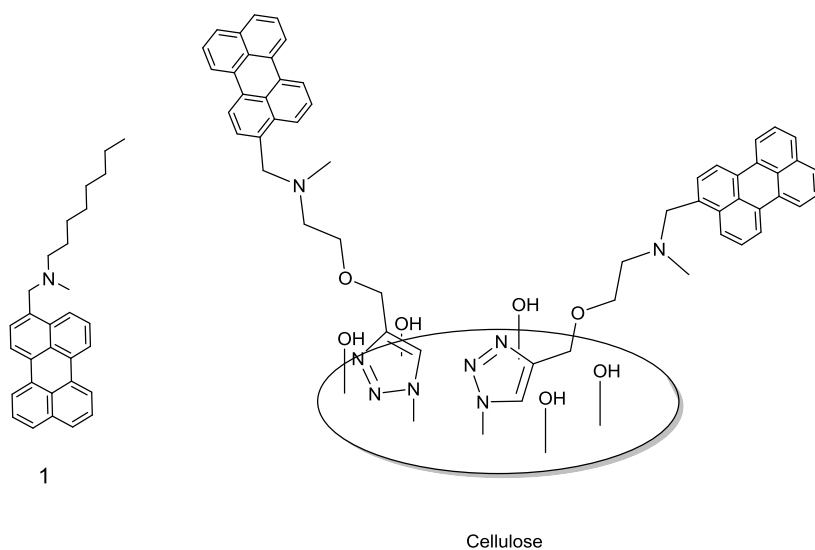
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Au cours des dernières années, le développement de matériaux intelligents demeure d'un intérêt croissant dans des domaines aussi divers que la réalisation de capteur ; le marquage de documents contre la contrefaçon¹. Parmi les matériaux disponibles, les composés biosourcés à base de cellulose offrent de nombreux avantages du fait de leur faible coût, de leur stabilité et de la fonctionnalisation.² Dans le domaine des capteurs, le suivi du pH demeure d'une plus grande importance en biologie³ ou pour le suivi de matériaux en particulier pour le suivi du pH à la surface de béton.⁴ Dans ce contexte Des matériaux à base de perylène incorporés dans des matrices de polymère de type hydrogel ont été développées pour la réalisation de capteur de pH.⁵ Une modulation de la fluorescence a été observée en fonction du pH du fait de la modulation des propriétés de transfert d'électron photoinduit. Dans cette communication, nous présentons la modulation de propriétés photophysiques de matériaux à base de cellulose greffés avec des fluorophores de types perylènes en fonction du pH.



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Circularly-Polarized Electrochemiluminescence

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Circularly polarized luminescence (CPL) is a very hot topic ^[1]. CPL is observed when the emission of left- and right-handed polarized light is unbalanced. CPL is a very useful technique to probe chiral systems in the excited states. Therefore, it is very complementary to circular dichroism (CD), which enables a ground state characterization.

Electrochemiluminescence (ECL) is observed when a luminophore is excited following an interfacial electron transfer step. In other words, it is an electrochemically-triggered luminescence process ^[2]. The main research activities in ECL concern the discovery of new ECL-active dyes and the development of analytical sensing based on ECL transduction.

Here, we report the proof-of-principle of circularly-polarized electrochemiluminescence (i.e. CP-ECL) based on two different molecular systems. The first one involves the classic and widely used tris(bipyridine)ruthenium(II) coordination complex with tri-*n*-propylamine (TPA) co-reactant ^[3]. In the second example, a bispyrene scaffold mounted on a constrained polyether macrocycle is employed as luminophore in combination with benzoyl peroxide (BPO) ^[4].

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Stabilizing and enhancing the properties of copper(I) photosensitive complexes by entrapment in silica nanoparticles

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Heavy metal complexes as photosensitizers dominate the world of photochemistry because they are versatile compounds, endowed with high photo-stability, and long-lived strong luminescence. This is why many luminescent systems (e.g. sensors, display devices) are based on those complexes, despite their high cost and toxicity. Nowadays, the trend is to replace heavy metal-based photosensitizers with low cost, yet performant, photosensitizers. In this regard, copper(I) complexes have demonstrated their quality in several instances. However, those complexes show a few drawbacks: in particular, the coordination sphere is labile (meaning that the complexes are easily destroyed when put in presence of some other exogenous ligand, or in presence of strong acids) and their photophysical properties are severely affected by the external medium (for example, the excited state of Cu(I) complexes is strongly quenched in coordinating solvents like acetonitrile or water). In order to solve all these issues, encapsulation of copper(I) complexes inside silica nanoparticles can be envisioned: when tightly bound to a silica matrix, through covalent bonds, the copper(I) complexes would be unprecedentedly stabilized and afford silica nanoparticles featuring the properties of copper(I) complexes: strong absorbance in the visible, excited state reactivity and near IR luminescence.

We focus on homoleptic copper(I) complexes CuL_2^+ where L is a phenanthroline ligand. To promote the excited-state properties we have synthesized phenanthroline (phen) ligands substituted with bulky groups at the 2- and 9-positions. In our case, to ensure that the copper(I) complexes are immobilized inside the silica shell, we functionalized phen ligands with 3-(Triethoxysilyl)propyl isocyanate in positions 2 and 9 of phen. The resulting functionalized copper(I) complex is mixed with organic soluble silica precursor tetraethoxysilane and the hydrolysis-condensation of all alkoxy silanes starts simultaneously, yielding a doped stable copper complex-silica hybrid material. Although the molecular complex **C1** is not luminescent [1], the obtained nano-objects **C1@SiO₂** are stable and feature long-lived luminescence, unravelling the relevance of our strategy.

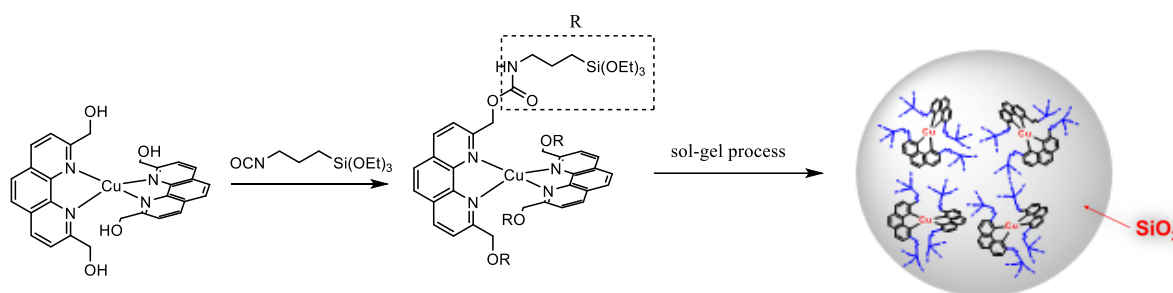


Figure 1. Overview of this work.

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Redefining the trade-off relationship between H-bonds and dispersive interactions in cooperative supramolecular polymerization

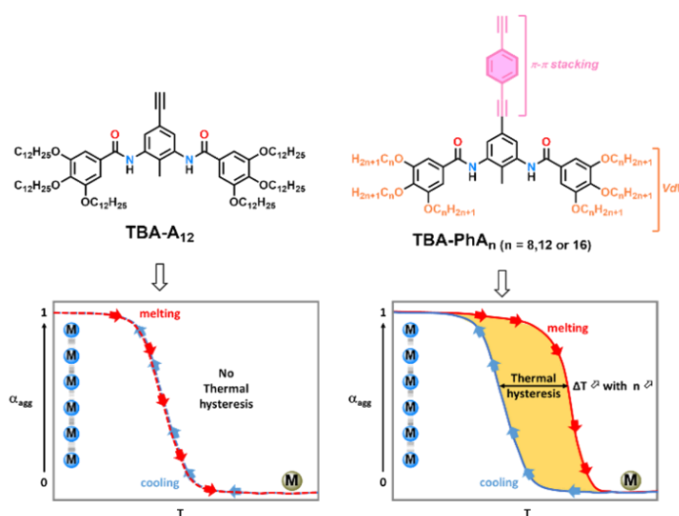
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One dimensional (1D) self-assembly of small molecules via supramolecular polymerization (SP) provides an appealing route toward (multi)functional conducting fibers or photo-active nano-assemblies.^[1] In those 1D materials, the small molecule monomers are tightly bound together by reversible and highly directional non-covalent interactions, such as hydrogen bonds, π - π stacking or interchain interactions to name a few.^[2] Their inherent high dynamicity ensures that the polymeric growth typically occurs under thermodynamic control. Conversely, kinetic effects do emerge in supramolecular polymerization when monomers are strongly interacting with each other in aggregates that differ from the thermodynamic one, or in an intramolecular way.^[3] This allows the monomers to be confined into energy traps as dormant states, lying at higher energy than the global thermodynamic minimum state and results in delaying the spontaneous polymerization, thereby leading to the opening of a thermal hysteresis in the plot of the aggregation parameter α_{agg} vs T. Very recently, Wang et al.^[4] reported the ability of π - π stacking interactions to also promote a kinetically metastable driving the SP of donor-acceptor aromatic molecules. However, a strategy enabling fine tuning of the thermal hysteresis by dispersive forces interplay is yet to be achieved. In this work, we demonstrate thanks to VT-UV/Vis and VT-DLS technics, that precise chemical engineering of dispersive forces balancing hydrogen bonding allows the control of the SP.^[5]



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Hexaphyrin-Cyclodextrin Hybrids: Redox Switching between Möbius and Hückel Aromatic Systems in Chiral Environment

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Hexaphyrins offer a versatile platform for aromaticity switching through multiple stimuli (redox, coordination, protonation, temperature, polarity and conformational constraints).^[1a-c] Remarkably, we recently showed that the association of an hexaphyrin to a doubly-linked chiral cyclodextrin unit (HCD) provides us with two 28π diastereomeric Möbius systems with opposite bridging pattern. Focusing on a dynamic strategy, metalation of these Möbius hexaphyrin with Zn(II) shows chirality transfers between the cyclodextrin, the bridging pattern and the hexaphyrin, tuning the *P/M* twist stereoselectivity up to 60% *de*.^[2] Following a different approach, Osuka group achieved metalation with Pd(II) binap salt, resulting in 23% *ee* and further enabling chiral separation.^[3] In order to obtain potentially resolvable diastereomers, metal coordination with Pd(II) was done on HCD systems which gave us two *pseudo* enantiomeric monometallic complexes (PdHCD) F1 and F2 with induced chiral communication from the cyclodextrin to the Möbius twist. These conformationally stable isomers allow to easily switch between Möbius and Hückel aromatic systems to develop new applications using planar chirality for chiral guest recognition and chiral sensing material.

28π Möbius aromatic PdHCD conjugates showed intense ECD (Electronic Circular Dichroism) spectra. The 28π PdHCD F1 and F2 *pseudo* enantiomers which show the same ECD spectra with opposite Cotton effects and large $\Delta\epsilon$ attributed to the strong aromaticity, is interesting in view of their potential application as chiral sensors. Redox tuning of chiroptical properties was achieved both with chemical and electrochemical oxidation, to form 26π Hückel aromatic PdHCD conjugates. The 26π PdHCD shows weaker ECD spectra for both F1 and F2. The stability of the chiroptical response between Möbius and Hückel aromatic systems allowed us to switch between these states up to 25 cycles. These promising results suggest to further investigate these systems with the redox process, chiral properties, host guest chemistry within confined space and further.

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Electrochemiluminescence Imaging of the Permeabilization of Single Giant Liposomes

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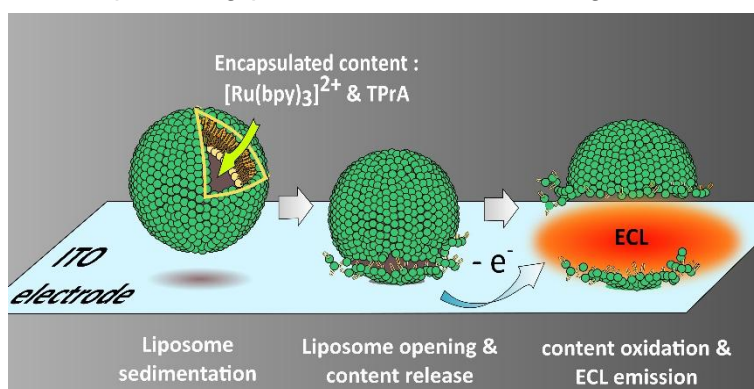
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Combining electrochemistry and luminescence offers the opportunity to study biological processes, such as the monitoring and quantification of transmembrane trafficking [1, 2]. In this context, we recently developed an electrochemiluminescence (ECL) imaging strategy to characterize the release events from liposomes (Figure 1) [3]. The strategy consisted first in the encapsulation of ECL reagents ($[\text{Ru}(\text{bpy})_3]^{2+}$ and tripropylamine (TPrA)) in sealed giant asymmetrical liposomes (100 μm in diameter) made of DOPG/DOPC phospholipids. Then, liposome permeabilization was triggered at the surface of a polarized transparent ITO electrode, allowing the electrochemical oxidation of the content and the visualization of the leaking process. The simultaneous ECL, photoluminescent and amperometric monitoring provided information on the liposome shape during permeabilization, the assignment of the corresponding signals to a specific liposome, as well as the quantification of the TPrA released. This original approach was recently successfully used to image the permeabilization of liposomes by melittin, a representative antimicrobial peptide (AMP) [4].



F

figure 1. ECL imaging of single giant liposomes opening at polarized electrodes.

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Booklet of Abstracts

Poster presentations

Charge transport properties in nanohoops

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In the last ten years, the development of π -conjugated nanohoops has been considerable owing to their remarkable properties.^[1]

However, to date, their incorporation in organic electronic devices remains very scarce and their performance is low.^[2] This could be linked to their weak charge transport

properties.^[3] In order to increase the efficiency of the nanohoops based organic semiconductors, their charge transport properties should be first studied.^[4] Thanks to a structure-properties relationship study centred on the cyclic tetracarbazole substituted by butyl chains, we evaluate the impact of:

- the cyclic geometry (by comparison with the linear tetracarbazole),
- the number of building units in the nanohoop (by comparison with the cyclic pentacarbazole),
- the presence of the bridgehead (by comparison with the [8]cyclo-*para*-phenylene),
- the length of the alkyl chains borne by the bridgehead (by comparison with the cyclocarbazole substituted by hexyl chains).

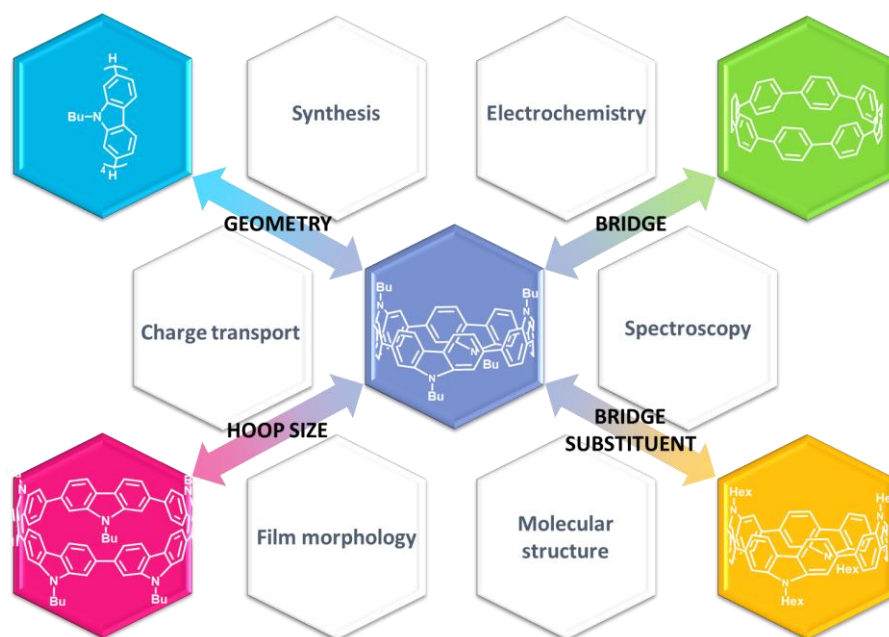
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Excited-State Intramolecular Proton Transfer chromophores and push-pull boron complexes based on pyrimidine core

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Keywords: Pyrimidine; Boron complexes; Photoluminescence; Anti-counterfeiting; ESIPT

Summary: Excited-State Intramolecular Proton Transfer (ESIPT) consist of a tautomerization in the excited state, leading to a proton transfer from a heteroatom to another. ESIPT chromophores are known for their environment-sensitive optical profiles and dual panchromatic emission can be observed in case of partially frustrated ESIPT.^[1] Such chromophores are usually constituted of a phenol fragment linked to a heterocycle. Recently, some pyrimidine-based ESIPT chromophores exhibiting acid vapor induced emission have been described for anti-counterfeiting applications.^[2] ESIPT chromophores can also be used for the synthesis of a boron complex, also displaying interesting luminescence properties.^[3]

In this communication, we will describe the synthesis and photophysical properties of a series of pyrimidine-based ESIPT chromophores and their boron complexes bearing various substituents (from moderate electron-withdrawing to strong electron-donating ones). For some chromophores ligands, acidification leads to the appearance of emission properties by frustration of ESIPT. Boron complexes are characterized by a strong intramolecular charge transfer when substituted by strong electron-donating groups as indicated by large emission solvatochromism.

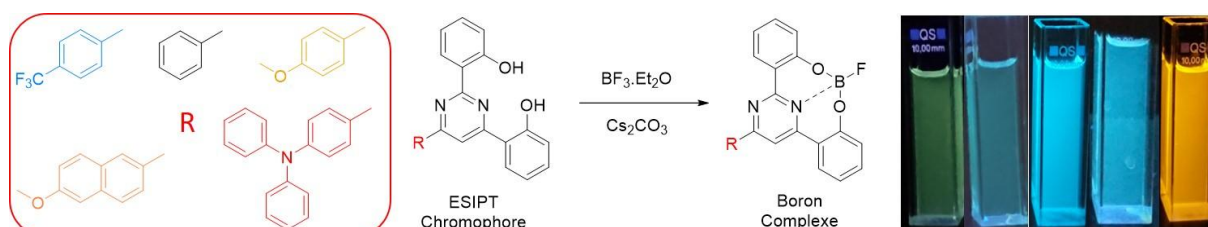


Fig. 1 Molecular structures of the ESIPT chromophores and their corresponding boron complexes. Photoluminescence of boron complexes in CH_2Cl_2 solution.

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Exploring structural and optical properties of soft salts based cyclometalated platinum complexes

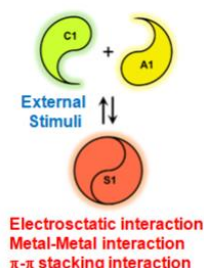
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Luminescent materials exhibiting reversible change in their optical properties under different external stimuli have huge application potentials in various optoelectronic fields. Thus, small molecules, metal complexes, and polymers have been developed as materials with photochromic, mechanochromic, vapochromic, electrochromic, and thermochromic properties. Due to their high photoluminescence quantum yields (PLQY), remarkable photostability, easy tunability of the emission wavelength, and increased sensitivity to external stimuli, Platinum(II) complexes are potential candidates for constructing stimuli-responsive luminescent materials.^[1]

Among them, soft salts based on ion-paired cyclometalated platinum(II) complexes are attracting increasing interest as potential candidates for the construction of stimulus-responsive luminescent materials. These complex salts (S1) showed original optical properties due to Pt(II)···Pt(II) and π - π stacking interactions between anionic (A1) and cationic (C1) complexes enabling selective response to various external stimuli by precisely regulating various intermolecular interactions.^[2]



In this communication, we will present the synthesis of a series of soft salts based on two oppositely charged cyclometalated platinum complexes **S1-9** ($[\text{Pt}(\text{C}^{\wedge}\text{N})\text{ed}]^+[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{CN})_2]^-$). Appropriate combination of cationic and anionic components allows tuning the photoluminescence properties of the formed salts. The influence of various structural modification on their photophysical properties had been thoroughly studied (PLQY, AIEE...) and the structure properties relationships were highlighted. To demonstrate the potential anti-counterfeiting applications of these soft salt complexes, vapochromism studies have been successfully explored.

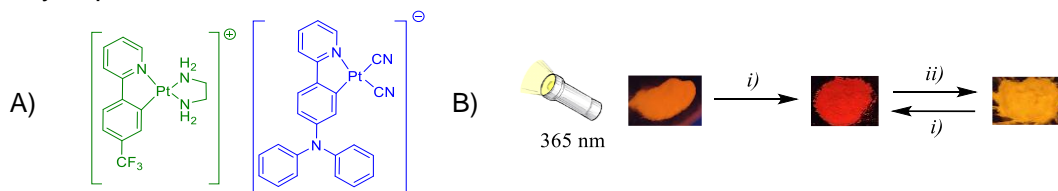


Figure: A) Structure of **S3**, B) Luminescence photos of reversible switching of the Ex-De emission using **S3** solid. Conditions: i) Vapor of MeOH, CH₂Cl₂, ii) Vapor of acetone, DCM, THF or grinding manipulation.

Acknowledgements

A.R. acknowledges the Région Bretagne, France and Conseil Départemental des Côtes d'Armor, France for his PhD funding

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Exploring Valence Tautomerism in Trinuclear Triphenylene Cobalt Complexes

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Switchable molecules exhibiting reversible changes in their physical properties are highly promising for diverse applications, such as data storage and sensors.^[1] Following our work on Ni₃ complexes,^[2] this study aims at designing trinuclear cobalt complexes based on the tris-bidentate bridging hexahydroxytriphenylene (H₆HHTP) ligand (Fig 1),^[3] capable of displaying multi-step electronic switching induced by temperature or light irradiation. In these complexes of general formula [M₃(L)₃HHTP]^{x+}, where M is a transition metal ion and L a tetradentate ligand, seven oxidation states of HHTP^{y-} are theoretically accessible, through reversible oxidations of the catechol (cat) species into semiquinone (sq), and to quinone (q). Using Co(II), we aim to induce valence tautomerism (VT), that involves an intramolecular electron transfer between a paramagnetic Co(II) centre and a redox-active semiquinone, leading to the diamagnetic Co(III)-catechol form (Fig 1). The key-point is, therefore, to prepare trinuclear complexes comprising the Co(II)-sq and/or the Co(III)-cat, achieved by adjusting the Co crystal field through the nature of the ancillary tetradentate ligand L.^[4] In this work, [Co₃(Me_ntpa)₃HHTP]^{x+} (n = 0-3) complexes have been prepared and characterized. Preliminary experiments revealed that [Co₃(Me₂tpa)₃HHTP]³⁺ undergoes a VT transition at 400K, attributed to the conversion of Co^{II}Co^{III}₂[cat cat sq]^{•3+} into Co^{II}₂Co^{III}[cat sq sq]³⁺, while [Co₃(Me₃tpa)₃HHTP]³⁺ is stabilized in the paramagnetic Co^{II}₃[sq sq sq]^{•3+} redox state.

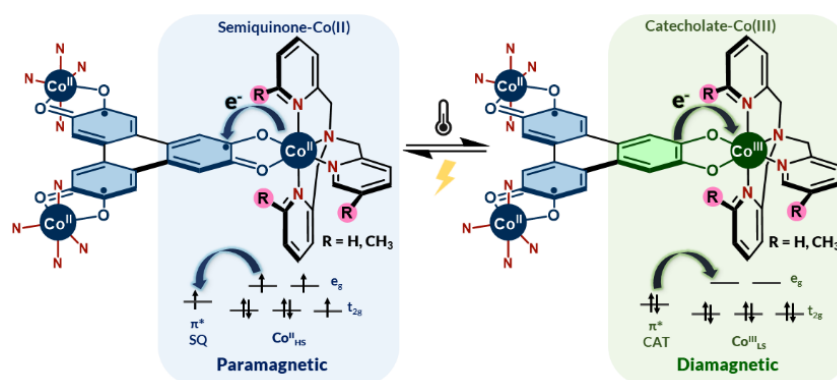


Fig. 1 Valence tautomerism in a [Co₃(Me_ntpa)₃HHTP]³⁺ complex.

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Investigating and linking different organic emitters to target self-organized metamaterials

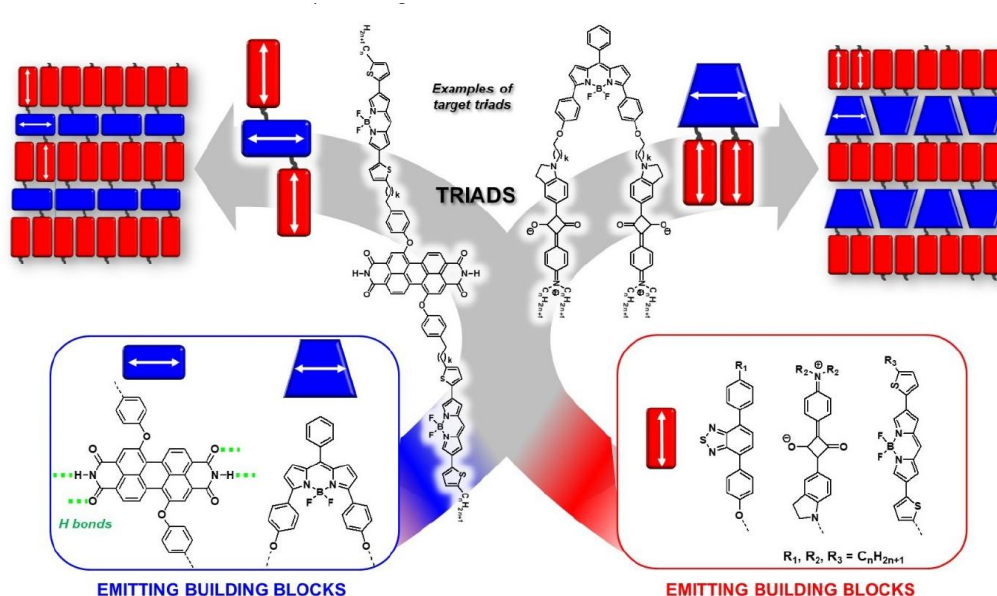
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In the context of luminescent organic material market growth, it is necessary to control different material parameters (phase and energy density flow). To do that, hyperbolic metamaterials (HMMs) have been developed. The research in this field increased mainly since 2010, with the rise of the publications number. Mainly composed of multilamellar inorganic components (metal and metal oxide), their making is a long multistep process. [1] Thus, we plan to make new organic HMMs presenting multilamellar liquid crystal behavior, to have better control of the order in one single-step processing method.[2] In this context, the synthesis of different TRIADS has been envisioned, one challenge (among others) in these assemblies being to control an orthogonal orientation of the dipolar transition moment of both emitters involved (see blue and red rectangle below). More precisely, in this presentation, we will discuss the choice and the first results related to PDI-BDPs TRIAD, BODIPYs (as a red rectangle) affording both a great luminescence tunability and very high quantum yields (PLQY), PDI dyes (as a blue rectangle) showing as well similar properties but also additional ones, such as self-assembly abilities and great luminescence in solid states.



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ORR Electrocatalysis: Playing with the Interface at the Molecular level

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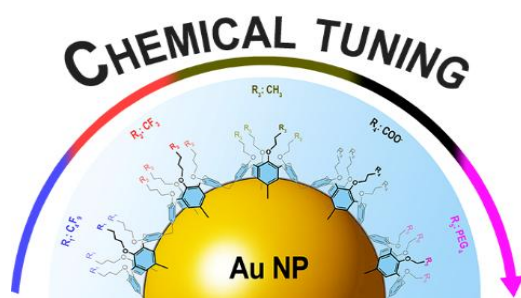
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The manipulations of size, of shape or of composition by topmost engineering with foreign metals of the nanomaterials is currently exploited to tune the reactivity and selectivity of the catalytic systems. Such manipulations are very often achieved thanks to small molecules or polymers acting as capping agents able to regulate the size and shape during the synthesis and to prevent from aggregation. But the organic capping agents are generally undesired at the catalytic surface because they are considered as inert species hiding the active sites on the nanoparticle catalyst. Thus, additional effort has to be made for the removal of organic ligands prior to use, without altering the material structure or morphology.

However, the promoting effects of ligands on heterogeneous catalysts have recently emerged, and a number of studies has shown that surface ligands can actually enhance the selectivity, activity and/or durability, notably in important electrocatalytic reactions including hydrogen evolution reaction (HER), carbon dioxide reduction reaction (CO₂RR) or oxygen reduction reaction (ORR).^[1]

The influence of organic modifiers is generally attributed to electronic or geometric (steric hindrance) effects that modify the adsorption/desorption processes; orientation of intermediates with respect to the catalytic surfaces.

Herein, we explore the effect of ligand tail groups at the solid/liquid interface in the



ORR electrocatalysis. Through diazonium chemistry, calix[4]arene macrocycles are grafted at the gold nanoparticles' surface. Sharing the same anchoring function and a common backbone, the calix[4]arene ligands possess distinct terminal chemical functions where the length, hydrophobic nature and oxygen affinity are varied, allowing to only focus on the molecular tuning of the solid/liquid interface through the change of the tail groups while

electronic effects which are regulated by the anchoring function will be similar for all catalysts. Beyond a pure geometric steric effect, we show that chemical properties of the ligands could effectively tune the interactions between the metallic catalyst and the electrolyte and reactants.^[2]

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Rhenium binuclear complexes with original solid-state emission properties: Are two complexes better than one?

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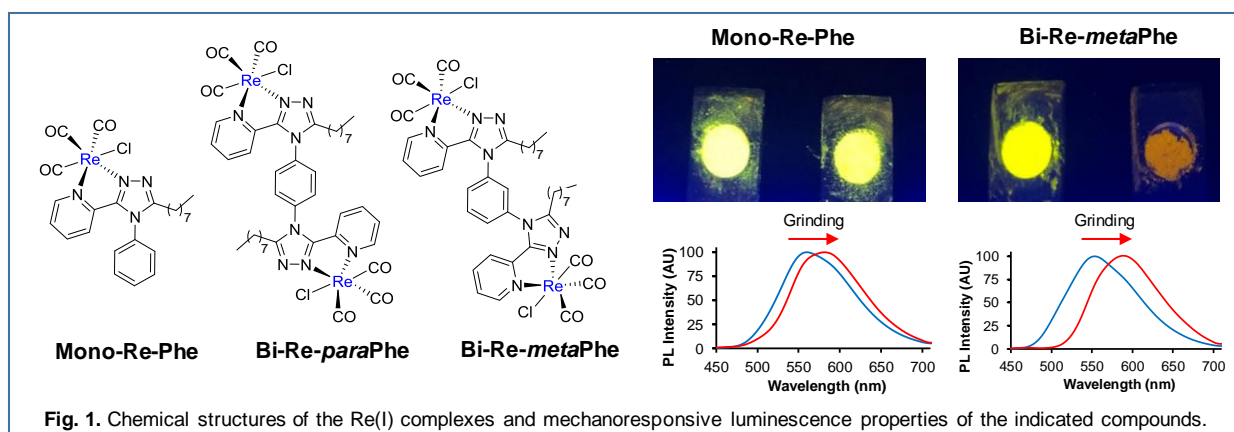
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Due to their stability, low toxicity and attractive spectroscopic properties, tricarbonylrhenium(I) complexes are popular bioimaging agents and sensors.^[1] Recently, our team has developed original mononuclear Re(I) complexes, potentially useful for applications in the field of photoluminescent materials. They show strong aggregation-induced emission (AIE)^[2] and unprecedented mechanoresponsive luminescence (MRL) properties.^[3] In this context, binuclear rhenium(I) complexes have scarcely been studied. However, according to the nature of the bridging ligand, major changes in geometry, electron system and intermolecular interactions can be expected, resulting in new physicochemical properties.

The new binuclear tricarbonylrhenium(I) complexes (**Bi-Re-paraPhe** and **Bi-Re-metaPhe**, Fig. 1) differ by the position of their (3-(2-pyridyl)-1,2,4-triazole) moieties on the central phenyl ring. It is shown that isomerism induces distinct spectroscopic behavior. The comparison with parent mononuclear complex **Mono-Re-Phe** highlights the advantage of the binuclear structure regarding the photoluminescence properties. This study is a first step toward the design of binuclear Re complexes with efficient AIE and MRL properties.



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Mechanochromic luminescence properties of copper iodide complexes

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Stimuli-responsive luminescent materials are attracting particular attention because of their wide range of potential technological applications.^[1] Among them, mechanochromic luminescent materials characterized by a reversible change of the emission wavelength in response to external mechanical forces, are good candidates for the development of memory-recording devices and motion or damage sensors.^[2] Because of their rich optical properties combined with economic advantages of copper element, copper(I) iodide complexes are particularly appealing for developing functional light-emitting materials.^[3]

We report our investigations regarding the mechanochromic luminescence properties of materials based on copper iodide complexes. As shown in the figure, the photoemission properties of these compounds can greatly be modified upon mechanical stimulations.^[4-6] The origin of the mechanochromism has been both experimentally and theoretically investigated. Comparative studies of different crystalline polymorphs permit the establishment of structure-properties relationships giving additional insights into the mechanochromism mechanism. These compounds can also present temperature-dependent luminescence properties, an appealing feature toward the development of multifunctional materials.

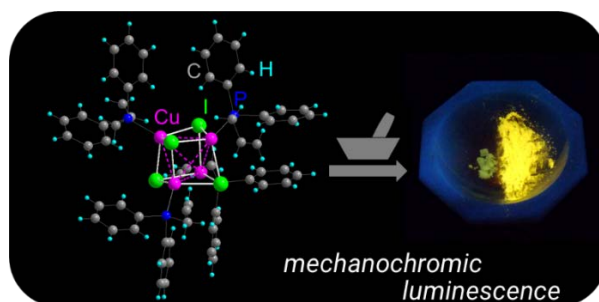


Fig. 1 Molecular structure of a polynuclear copper iodide complex and its partially ground crystalline powder.

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NEW DITHIENYLETHENES – POLYOXOMETALATES SUPRAMOLECULAR ASSEMBLIES WITH FAST SOLID-STATE PHOTOCROMIC PROPERTIES: COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDIES

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The family of dithienylethenes (DTE) is known for its excellent photochromic behavior in solution,^[1] but has shown limitation in the solid state in terms of complete, fast and reversible photoswitching. In particular, some of DTE crystals demonstrate breaking with high photoconversion yield, which makes structural analysis complicated.

Very recently, we have elaborated the first crystallized supramolecular assembly of polyoxometalates^[2-3] (POMs), which are nanosized anionic metal-oxide clusters, with a normal DTE (Fig. 1).^[4] This coupling modifies the photoresponse of the organic switch via both steric and electronic effects, and gives rise to an increased cycloreversion rate, resulting in a fast and complete re-opening process. The crystal structure after UV-light irradiation contains a mixture of open- and closed-ring DTE isomers with a conversion rate of about 28% which represents one of the highest conversions for a DTE-based material. Geometry optimization and electronic structures have been performed by ab initio DFT calculations to improve the structural model and nicely model the solid-state optical properties.

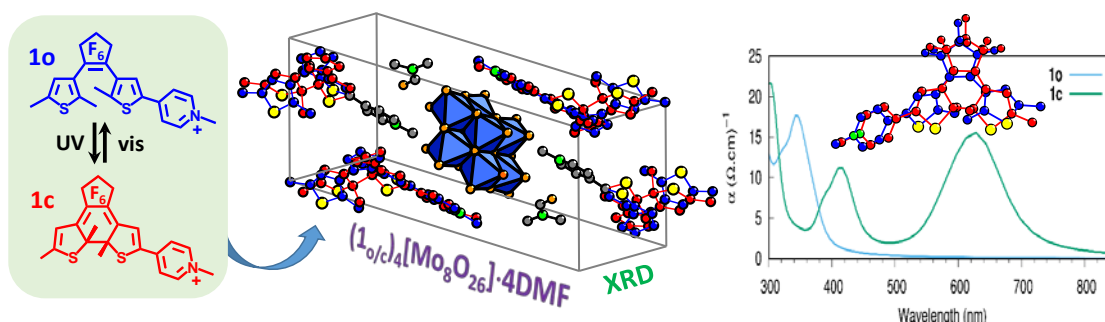


Fig. 1 Crystal structure of $(1_o/c)_4[Mo_8O_{26}] \cdot 4DMF$ after irradiation upon linearly polarized 365 nm light, and DFT rationalization of its optical properties.

Five other hybrids have been also designed by associating normal or mixed DTEs with different POMs.^[5] Combined X-ray crystallographic and spectroscopic analyses have highlighted the impact of organic and inorganic components on the photoswitching ability of the assemblies.

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