



La subdivision Photochimie, Photophysique et Photosciences (SP2P, Division de Chimie-Physique, SCF) et la Société Française de Photobiologie (SFPb), organisent conjointement leur réunion annuelle :



PHOTOSCIENCES, PHOTOBIOLOGIE DANS TOUS LEURS ETATS Grenoble 21-23 Mai 2024

Keynote speakers:

Nathalie Destouches (Université St Etienne)
Angela Falciatore (Sorbonne université)
Celine Frochot (Université de Lorraine)
Christian George (IrcelLyon)

Invited Talks:

Zacharias Amara (CNAM, Paris)
Stéphanie Bonneau (Sorbonne université)
Renaud Demadrille (IRIG-CEA Grenoble)
Massimo Trotta (Universita di Bari (It.))

<https://photosciences24.sciencesconf.org>

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Photosciences'24

Tuesday May 21 2024

13h45 → 14h10: welcome/ introduction

14h10 → 14h50: Keynote 1: Angela Falciatore, IBPC Paris

Light sensing in marine phytoplankton

14h50 → 15h10: OC 1 E. Simon, ENS Paris Sorbonne

Near-infrared co-illumination of fluorescent proteins reduces photobleaching and phototoxicity

15h10 → 15h30: OC 2 T. Beguin, Paris Saclay

UV-Vis spectroscopy and mass spectrometry synergy to pinpoint mutations that can improve the photostability of fluorescent proteins

15h30 → 15h50: OC 3 J. Wulffelé, CEA Grenoble

The complex photophysics of photoconvertible fluorescent proteins under 405-nm illumination

15h50 → 16h10: coffee break

16h10 → 16h40: Invited Talk 1. Zacharias Amara, CNAM Paris

Interfacial Control of visible-light photochemical reaction with immobilized photosensitizers

16h40 → 17h00: OC 4 D. Frath, ENS Lyon

Photoredox Control of Electron-responsive and Conductive Supramolecular Materials Based on Viologens

17h00 → 17h20: OC 5 L. Favereau, Rennes

Room Temperature Phosphorescence in Purely Organic Chiral Molecular Materials

17h20 → 17h40: OC 6 N. Fabre, CEA Paris-Saclay

Photonic properties of a perylenediimide monolayer assembled by the Langmuir-Blodgett technique

17h40 → 18h00: OC 7 C. Duranteau, Nancy

“DCM-like” fluorophores conjugated to thermoresponsive polymer: toward thermometric photothermal agent

Wednesday May 22 2024

9h20 → 10h00: Keynote 2: Christian George, IRCELYON

Photosensitization in the air... and its impact on oxidation capacity

10h00 → 10h20: OC 8 A. Nhari, CEA Grenoble

Carbazole-based lanthanide luminescent bioprobes for live cell imaging and Reactive Oxygen Species sensing

10h20 → 10h40: OC 9 M. Hojorat, Rennes

Helical donor-acceptor Platina[5]helicenes Complexes for Dual Luminescence and Near-infrared Circularly Polarized Luminescence

10h40 → 11h: coffee break

11h00 → 11h30: Invited Talk 2 R. Demadrille, CEA Grenoble

Push-pull photochromic dyes for use in semi-transparent solar cells with dynamic optical properties

11h30 → 11h50: OC 10 P.A. Bouit, Rennes

Introducing P in cyanine dyes: smells like polymethine spirit?

11h50 → 12h10: OC 11 A. J. Riquelme, CEA Grenoble

Tuning Optoelectronic Properties of Photochromic Dye-sensitized Solar Cells Through Molecular Engineering

12h10 → 14h00: Lunch on site

14h00 → 14h40: Keynote 3: C. Frochot, Univ. de Lorraine

Targeting to improve the efficacy of photodynamic therapy

14h40 → 15h00: OC 12 J. Couvez, Bordeaux Hydrophilic Biocompatible Fluorescent Organic Nanoparticles as Nanocarriers for Biosourced Photosensitizers for Photodynamic Therapy
15h00 → 15h20: OC 13 P. Changenet, Ecole Polytechnique Light-driven control of G-quadruplex DNA structures with non-covalent azobenzene derivatives
15h20 → 15h40: OC 14 D. Verga, Saclay Spatiotemporally controlled Photoaffinity Labelling of nucleic acid secondary structures
15h40 → 16h00: coffee break
16h00 → 16h30: Invited Talk 3 S. Bonneau, Univ. Paris Sorbonne Deciphering Real-Time Mitochondrial Dynamics: Impact of Photo-Oxidative Stress on Lipid Membranes
16h30 → 16h50: OC 15 A. Ntadambanya, Saclay Quantum-dot based nanosensors to study focal adhesion. Assembly and mechanosensing
16h50 → 17h10: OC 16 M. Erard, Saclay Förster Resonance Energy Transfer combined with Fluorescence Lifetime Imaging: a winning combination for exploring membrane contacts in cellulose
17h10 → 17h30: OC 17 C. Elian, Créteil Using visible light for bacterial decontamination of bio-based materials
17h30 → 17h50: OC 18 H. Hayek, Créteil Innovative photosensitizers for sustainably engineered polymers with advanced antibacterial properties
17h50 → 19h00: Poster session
19h30 → Diner on site

Thursday May 23 2024
9h00 → 9h40: Keynote 4: N. Destouches, Saint Etienne Laser-induced transformation mechanism of plasmonic Ag nanoparticles in TiO₂ and applications
9h40 → 10h00: OC 19 A. Khitous, Mulhouse Integration of sol-gel TiO ₂ thin film on gold nanoparticles for heterogeneous plasmonic photocatalysis
10h00 → 10h20: OC 20 C. Molinaro, Mulhouse Polymerization induced through the heat generation of gold nanoparticles under pulsed and continuous laser illumination
10h20 → 10h40: OC 21 J. Christmann, Clermont-Ferrand Etude spectroscopique de la perméabilité en phase liquide du polyéthylène au cours de son photovieillissement
10h40 → 11h00: coffee break
11h00 → 11h30: Invited Talk 4 M. Trotta, Univ. Bari Never green enough. Photosynthesis from the planetary to the nanometric scale.
11h30 → 11h50: OC 22 J. Fortage, Grenoble Ru tris-diphenylsulfonate-phenanthroline is a good challenger to the [Ru(bpy) ₃] ²⁺ sensitizer with for light-driven H ₂ evolution in water
11h50 → 12h10: OC 23 D. Mirani, CEA Grenoble Effect of electrolyte additives on the performance of photochromic dye sensitized solar cell
12h10 → Closing of the congress. Communications awards ceremony

Tuesday May 21 2024

Light sensing in marine phytoplankton

Angela Falciatore

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Phytoplankton are microscopic aquatic organisms, responsible for about half of the photosynthetic activity on Earth. Over the past two decades, breakthroughs in genomics and ecosystem biology, as well as the development of genetic resources in model species, have redrawn the boundaries of our knowledge of the relevance of these microbes in global ecosystems. However, considering their vast biodiversity and complex evolutionary history, our comprehension of algal biology remains limited.

Our major interest is in understanding the biology of the diatoms, one of the most prominent groups of phytoplanktonic organisms, standing at the crossroads of several evolutionary lineages. Diatoms are found in marine and freshwater environments, but also in soils, rocks and ice, and show remarkable phenotypic diversity at the cellular, physiological and metabolic levels, and a variety of life cycles and lifestyle traits. It is well established that diatoms have developed highly effective systems for optimizing light harvesting and energy generation from photosynthesis. However, still very little is known on the role of light sensing in the acclimation mechanisms, which synergistically control growth and distribution of diatoms within the ecological niches and oceanic provinces they inhabit. In the last years, the systematic use of genome-enabled approaches has revealed a plethora of blue light cryptochrome and aureochrome photoreceptors in diatoms. Even sensors usually responding in red and far-red region of the light spectrum, e.g., Phytochrome (DPH) have been described, despite their spectral characteristics make their presence counterintuitive in the red absorbing water column. By characterizing photoreceptors of diverse diatom model species and by assessing their distribution and possible activity in the environment, our analyses indicate that light-driven processes are key players of diatom functional biodiversity. These findings also emphasize that integration of laboratory and environmental studies, and dialogues between different scientific communities are both timely and essential to understand the life of phototrophs in complex ecosystems and to properly assess the consequences of environmental changes on aquatic environments globally.

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Near-infrared co-illumination of fluorescent proteins reduces photobleaching and phototoxicity

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We will present a new method to reduce the photobleaching of fluorescent proteins and the associated phototoxicity. Our method exploits a photophysical process known as reverse intersystem crossing (RISC) to depopulate the triplet excited state of fluorophores, a precursor to photobleaching and a source of reactive oxygen species. We achieve RISC by co-illuminating the fluorophores at a near-infrared wavelength absorbed by their triplet excited state, during their excitation with visible light. We will show that this dual illumination method can be successfully applied to wide-field fluorescence imaging and that it works in live eukaryotic and prokaryotic cells with a wide range of fluorescent proteins, leading to a typical 4-fold reduction in photobleaching. Our method can, for example, substantially improve the monitoring of fluorescently-tagged replisomes in *E. coli*. A direct comparison with classical antifading media shows that dual illumination is more efficient. It also has the advantage that it does not require any specific preparation of the samples before imaging. We will further show that dual illumination reduces the phototoxicity caused by fluorescent protein excitation in bacteria and primary mouse neutrophils, and that near-infrared light does not significantly perturb the cells. This makes our method particularly well suited for in vivo dynamical studies.

Acknowledgements

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UV-Vis spectroscopy and mass spectrometry synergy to pinpoint mutations that can improve the photostability of fluorescent proteins

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Fluorescent proteins (FPs) are genetically encoded fluorescent probes that have become invaluable in bioscience and biophotonics as they allow the understanding of biological processes at the molecular level in living cells. Unfortunately, the accurate monitoring of biochemical events is often limited by photobleaching, a gradual loss of fluorescence of FPs under light excitation, which affect both time and spatial resolution during image recording. Consequently, the improvement of FPs' photostability is a major challenge that requires a thorough understanding of the mechanisms involved in photobleaching¹. Some photochemical reactions and the residues involved have already been reported², but there is currently no systematic approach to get the full spectrum of potential photoproducts and their corresponding residues. This represents a crucial prerequisite for developing a rational mutagenesis strategy. This challenge arises from the diversity of photoreactions that a given FP can undergo, and which can deeply depend on the experimental conditions³. In addition, the kinetics and the proportions of those photoreactions may also vary from a FP to another².

Here, we report a whole analytical workflow combining biochemistry, UV-visible spectroscopy, mass spectrometry and kinetic modelling aiming to (1) describe the photochemical reactions (2) identify the residues involved in the photobleaching of YFPs, a family of FPs widely used in fluorescence microscopy and still in active development. First, we built a custom setup that allow both irradiation of aqueous solution of YFP with controlled irradiation densities and monitoring of absorption and fluorescence emission spectra over the time. From these experiments, we can extract the kinetic parameters of photobleaching and assess their changes under the modification of certain experimental conditions (e.g. nature of the YFP, concentration, light power, molecular oxygen presence...). In a second step, the detailed analysis of the photobleached samples by mass spectrometry (MS and MS/MS) provided insights into the chemical nature of the generated photoproducts.

This workflow confirms the presence of a diversity of photoproducts for EYFP, Citrine and some of their variants at position 69 and 145 and highlights significant disparities in kinetics and relative quantities of those identified photoproducts. However, two main different reactional pathways have been identified. The first one is heavily oxygen dependent and results in multiple oxidations of the FP, concomitant with the protonation of its chromophore. According to mass spectrometry analysis (MS/MS), the oxidations are mainly localized around the chromophore pocket, likely induced by the photosensitization of the chromophore with molecular oxygen, triggering various reactions on the surrounding residues. The second pathway lead to cleavage of the peptidic chain near the chromophore, leading to a non-absorbing state. These results are consistent with previous observations in the literature on individual fluorescent proteins of different colors sharing the same chromophore but possessing distinct protein sequences^{3,4}, thereby demonstrating the relevance of the workflow for obtaining a comprehensive understanding of photobleaching for YFPs and for other FPs in the future.

Acknowledgements

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The complex photophysics of photoconvertible fluorescent proteins under 405-nm illumination

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Fluorescent proteins (FPs) have become indispensable tools in biological research. Photoconvertible FPs (PCFPs) form a special class of FPs, able to convert from one fluorescent color into another when illuminated with near-UV light (~405 nm). Because of their photoconversion ability, PCFPs are widely used as markers for Single Molecule Localization Microscopy (SMLM). A key property of PCFPs is their photoconversion efficiency (PCE), i.e. the fraction of molecules that can be successfully photoconverted. A high PCE is crucial for obtaining a high spatial resolution (**Figure 1**). However, the PCE is strongly dependent on the illumination- and environmental conditions. A better understanding of the different factors that affect the PCE is important for the development of optimized experimental designs. In previous work, we showed that the PCE of the popular green-to-red PCFP mEos4b decreases as the 405 nm light intensity increases, due to non-linear bleaching of the Green state (**Figure 1**)^{1,2}. Recent studies suggest that, in addition, 405 nm light also negatively affects the photoconverted Red state of PCFPs^{3,4}. This latter issue will be emphasized during this presentation. I will show that, using a combination of NMR spectroscopy and fluorescence microscopy, 405 nm light induces the formation of a previously uncharacterized dark state. Recovery from this dark state is promoted by 561 nm light and O₂. The possible nature of this state and its consequences for SMLM will be discussed.

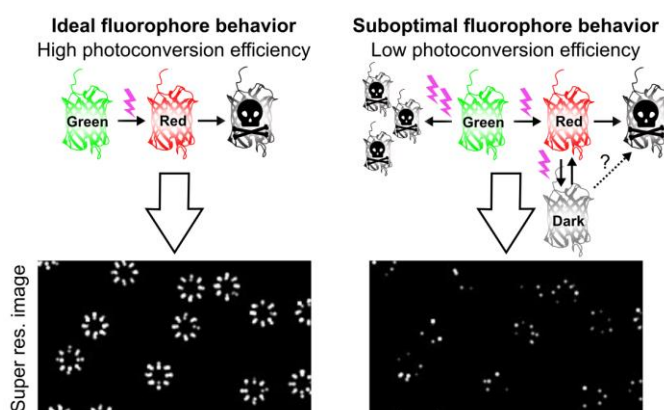


Figure 1. Suboptimal fluorophore behavior degrades image quality. Left: An ideal fluorophore with a high photoconversion efficiency gives a high-resolution image. Right: A suboptimal fluorophore with a low photoconversion efficiency gives a low-resolution image.

Acknowledgements

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Interfacial Control of Visible-Light Photochemical Reactions with Immobilized Photosensitizers

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By harvesting the energy of visible light, photosensitizers can activate a wide range of chemical reactions very selectively and produce a variety of high value compounds.^[1] However, despite these great potentials, their uses remain under-exploited in chemical manufacturing. This is usually explained by poor reaction efficiency and prolonged reaction times, which together generate prohibitive processing costs. Transposition of batch photochemical reactions into continuous flow reactors has proven to be a very attractive solution but improvements remain to be done to allow photochemistry to become a competitive technology at production scale.^[2]

In this presentation, we will discuss how this can potentially be approached at the molecular level, by disclosing our recent results on the performances of immobilized photosensitizers on solid supports for the design of greener photochemical oxidations. Our general approach focuses on the immobilization of photosensitizers on solid inorganic supports as a straightforward and inexpensive method to enhance catalyst reactivity and stability, while providing simple recycling options. We demonstrate that this optimization at the nano and micro-scale level provides interesting features in terms of physicochemical properties, which translates into enhanced reactivity using green solvents or no solvents at all.^[3] All these approaches are usefully transposed in continuous flow processes using home-made or commercial reactors resulting in an optimization at the macro-scale level.^[4] When combined, these factors hold great promises for the development of genuinely environmentally friendly and cost-competitive photochemical production.

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All the coworkers who have contributed to this work and the Molecular Chemistry Team at Cnam. Corning for the free loan of a LabPhoto reactor. Hepatochem for providing free-samples of phthalocyanines. Financial supports: ANR JCJC Red2Green, ANR TheoBioDye, Bill & Melinda Gates Foundation, French Embassy in Canada and ACS GCIPR.

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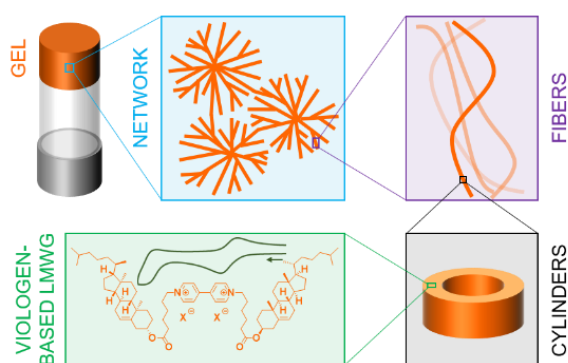
Photoredox Control of Electron-responsive and Conductive Supramolecular Materials Based on Viologens

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The key elements in the development of nanoscience are to observe, modify and control matter at the nanoscale. One strategy proposed to meet these immense challenges is to develop responsive molecular or supramolecular systems for which a structural reorganization is obtained in response to an external stimulation. By analogy to the term used in geology, such a behavior is known as *metamorphism*. Systems that endure structural changes leading to major modification of macroscopic properties are of great interest for the controlled capture and release of guest molecules, the development of molecular machines and molecular electronics. Our research efforts in this field have led us to focus on molecular and supramolecular architectures involving viologens (4,4'-bipyridinium salts) as key electron-responsive building elements.¹ In particular, we have developed different strategies allowing to exploit the ability of viologen derivatives to form π -dimers in their reduced state to achieve a remote control over their organization within supramolecular assemblies. Among our recent achievements, we have reported a sol/gel transition triggered by light-irradiation of a viologen-based coordination polymer formed in the presence of palladium ions.²



We now report supramolecular gels obtained by self-assembly of a dicationic low molecular weight gelator based on viologen. These molecules have been shown to self-assemble in pentanol to form chiral hollow core-shell cylinders eventually yielding dendritic clusters inducing gelation. We also showed that the optical, rheological and electrical properties of the gels can be tuned by addition of ionic additives. Careful control of the formation of charge-transfer complexes between viologens and iodides have led to a robust, transparent, conductive and chiral gel.³ Properties of this responsive material can be modulated when submitting it to electrical or light stimulation.

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Room Temperature Phosphorescence in Purely Organic Chiral Molecular Materials

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Room temperature phosphorescence (RTP) from purely organic compounds (*i.e.* without any metal), and related photophysical aspects linked to the management of triplet excited-states have become a crucial issue for several areas of research, ranging from optoelectronics, non-linear optics to photocatalysis, and bioimaging.¹ Recently, the possibility to obtain RT circularly polarized (CP) phosphorescence with chiral organic emitters has also attracted significant interest due to the potential access to different states of CP-light (either left or right).⁶⁻¹²

In this congress, I would like to present our contributions regarding this area of research, notably by illustrating how the enantiopurity of a chiral material offers a unique possibility to explore the impact of intermolecular interactions on the efficiency of photophysical properties and/or electronic conduction without altering its molecular electronic properties. Our findings show that comparing RTP between racemic and enantiopure crystals can bring further information on the intermolecular interactions impacting the triplet exciton stabilization and migration, which needs to be optimized for designing efficient organic RTP molecular materials.

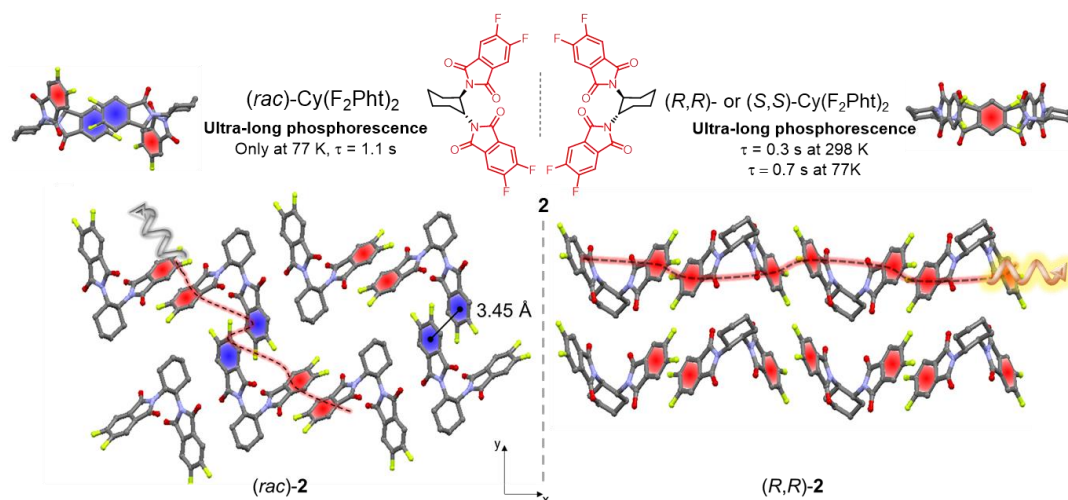


Figure: Chemical structures of *RR*-*Cy*(*F*₂*Pht*)₂ and *SS*-*Cy*(*F*₂*Pht*)₂; and comparison of their X-ray crystallographic structures at the molecular and supramolecular levels with different views of intermolecular interactions between dimers (red for H-type aggregates, and blue for J-ones).

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Photonic properties of a perylenediimide monolayer assembled by the Langmuir–Blodgett technique

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Two-dimensional (2D) materials are a class of materials with unique properties that have attracted significant attention in recent years. Unlike 3D materials, which have bulk properties that are governed by their crystal structure, 2D materials have properties that are strongly influenced by their size and shape. Preparation of 2D materials based on organic molecules is a key-point to obtain devices with uncommon photonic properties ¹

Herein, we focused on 2D materials based on perylene diimide derivatives. Our main goal was to prepare highly oriented 2D materials while also controlling molecules' orientation. We employed Langmuir-Blodgett technique to prepare 2D materials based on perylene diimide derivatives. Using Langmuir-Blodgett trough, we obtained single monolayers that demonstrated interesting photonic properties. Through micro-spectroscopy, we detected a charge transfer band that was characteristic of well-organized aggregated molecules. We also employed micro time resolved spectroscopy to understand and fully characterize the dynamics of the excited state. However, there are three possibilities for the orientation of molecules on the surface as display in Figure 1.

To fully characterize the orientation of the molecules, we developed an incidence angle-resolved spectroscopy method that provide valuable insights into the orientation of molecules on surface. Additionally, by analyzing the back focal plane, we obtained information about emission direction. These two techniques allowed us to conclude definitively on the orientation of the molecules on the surface. ²

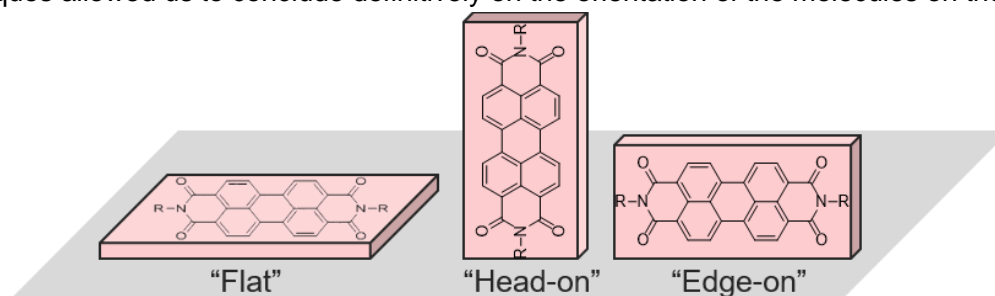


Figure 1. Possible orientation of the molecules on the surface.

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“DCM-like” fluorophores conjugated to thermoresponsive polymer: toward thermometric photothermal agent

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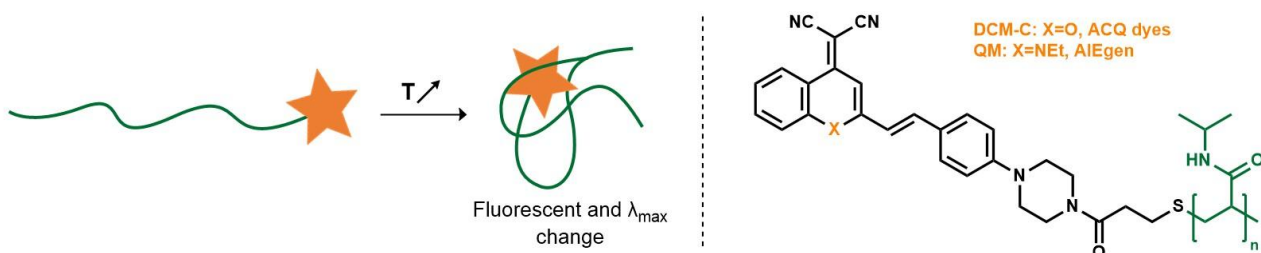
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Fluorescent molecular thermometers play a crucial role due to their significant potential in biomedical applications, particularly in temperature-feedback photothermal therapy (PTT). PTT, an evolving therapeutic technique, faces challenges related to precise temperature control to optimize therapeutic effects and minimize side effects. Consequently, there is a growing interest in photothermal agents capable of providing real-time temperature feedback through fluorescence imaging during irradiation.¹

“DCM-like” compounds are a family of push-pull fluorophores with environment-sensitive luminescence response. By varying the acceptor core, they can behave as "Aggregation Cause Quenching" (ACQ) or "Aggregation Induced Emission" (AIE) dyes, and gives polarity/viscosity-dependent response.² As we recently showed, they can also be effective as light-to-heat converters when fluorescence/photoisomerization deactivation channels are reduced.³

Furthermore, as a proof-of-concept, DCM-like compounds were covalently linked with a thermosensitive LCST (Lower Critical Solution Temperature) polymer capable of achieving phase-transition from a freely soluble to an insoluble state above a certain threshold temperature, hence triggering an abrupt modification of the dye's environment and thus of its luminescence properties. The nature of DCM-like compound was varied from dicyanomethylene-4H-chromene (DCM-C) to quinoline malonitrile (QM) in order to identify the most suitable mechanism (ACQ, AIE) to achieve an optimal readout of the threshold temperature by fluorescence. The fluorophores were attached at end-chain position of the thermosensitive poly(N-isopropylacrylamide) (PNIPAM) biocompatible polymer, and the fluorophore-polymer conjugates structures were confirmed by analytical methods (NMR, MS). Their temperature-dependent optical properties were evaluated by steady-state photophysical techniques, and showed significant fluorescence change upon passing the transition-phase temperature. These encouraging results serve as guide for the future design of thermometric photothermal agent with required properties for in vivo applications.



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Wednesday May 22 2024

Photosensitization in the air... and its impact on oxidation capacity

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This seminar is an invitation to think differently about the possible oxidation pathways occurring in secondary organic aerosols (SOA).

Despite the importance of aerosols in atmospheric chemistry, climate and air pollution, our ability to assess their impact on atmospheric physics and chemistry is still limited due to insufficient understanding of many processes associated with the sources of particles, their chemical composition and morphology, and evolution of their composition and properties during their atmospheric lifetime. Indeed, atmospheric aerosols can be viewed as a complex conglomerate of thousands of chemical compounds forming a system that evolves in the atmosphere by chemical and dynamical processing including chemical interaction with oxidants and sunlight.

A significant body of literature on photo-induced charge or energy transfer in organic molecules from other fields of science (biochemistry and water waste treatment) exists. Such organic molecules are aromatics, substituted carbonyls and/or nitrogen containing compounds – all ubiquitous in tropospheric aerosols. Multiphase processes have also been shown to produce light absorbing compounds in the particle phase. The formation of such light absorbing species could induce new photochemical processes within the aerosol particles and/or at the gas/particle interface. Therefore, while bulk phase aquatic photochemistry has recognized several of these processes that accelerate degradation of dissolved organic matter, only little is known about such processes in/on atmospheric particles.

This presentation will discuss photosensitization in the troposphere as having a significant role in SOA formation and ageing as studied by means of laser transient absorption spectroscopy, flow tube and simulation chamber experiments, all coupled to advanced analytical techniques. We will provide kinetic and mechanistic information on how photosensitization may introduce new chemical pathways, so far unconsidered, which can impact both the chemical composition of the atmosphere and might thus contribute to close the current SOA underestimation.

Carbazole-based lanthanide luminescent bioprobes for live cell imaging and Reactive Oxygen Species sensing

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Lanthanide(III) complexes have fantastic luminescent properties that make them very attractive for bioimaging. Classic lanthanide-based luminescent bioprobes require high energy excitation by UV-visible light (300-450 nm), which is absorbed and scattered by the biological tissues and causes photodamage^{1,2}. Indeed, for cellular imaging applications, working with both excitation and emission in visible or, even better, in the near infrared is preferred to avoid these problems. This can be achieved by using Europium(III) as a red emitter or Terbium(III) as green emitters and a light-harvesting antenna (to sensitize Eu³⁺ or Tb³⁺ luminescence) that presents two-photon absorption properties^{3,4}. During the past two years, we have developed a Eu³⁺ complex featuring a carbazole antenna that features interesting two-photon absorption properties. This complex was conjugated to a cell penetrating peptide (CPP), allowing its delivery to the cytosol. Despite a very low quantum yield (0.2%), this system was successfully used for two-photon imaging of living cells⁵. Now, our goal is to improve its optical properties and to develop novel responsive probes based on this first imaging probe.

In this presentation we will present you how we optimized the luminescence properties of this Eu³⁺ and Tb³⁺ complex by tuning the photophysical properties of the carbazole antenna. Indeed, to improve its luminescence properties, we need to suppress an unproductive photoinduced electron transfer between the carbazole antenna and Eu³⁺. This was achieved by introducing electroattracting substituents on the carbazole unit. We will describe the synthesis of the CPP conjugates of this new lanthanide complex, their luminescence properties and two-photon microscopy imaging with these probes.

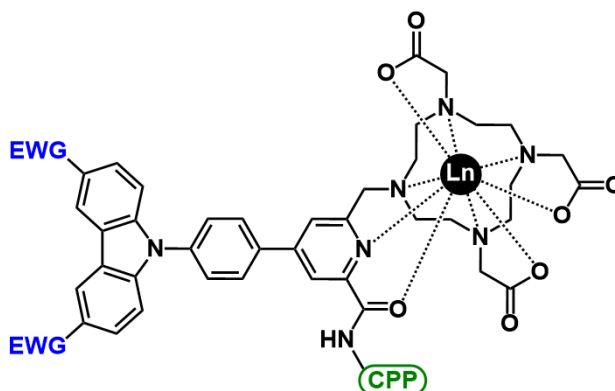


Figure : New two-photon luminescent lanthanide-based bioprobes with substituted cabarzoles.

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Helical donor-acceptor Platina[5]helicenes Complexes for Dual Luminescence and Near-infrared Circularly Polarized Luminescence

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The design of chiral π -conjugated materials that can manipulate circularly polarized light (CP-light) has recently attracted the attention due to their potential in numerous fields of technology, such as 3D display, sensors, information storage, spintronics, optoelectronic devices as well as in bio-imaging^[1]. Historically, chiral lanthanide complexes has been intensively investigated for their high CP luminescence (CPL) intensity with high dissymmetry factor ($g_{lum} = 2(L_L - L_R)/(L_L + L_R)$). Recently, chiral organic and organometallic materials have attracted more attention as CP-light absorbers and emitters due to their superior quantum yields (Φ) and readily tuneable photo-physical and chiro-optical properties^[2].

In this communication, I would like to present our recent results regarding the design of chiral platina[5]helicenes complexes based on donor-acceptor π -conjugated helical ligands. At ambient conditions, these Pt-complexes display far-red and NIR fluorescence and phosphorescence emissions, whose intensity being related to the intrinsic charge transfer character of the helical organic ligand. In addition, these complexes exhibit NIR CPL with considerable dissymmetry factor ($g_{lum} = 1.5 \times 10^{-3}$, Figure 1), affording an interesting molecular design to develop chiral emitters in this low energy region of the spectrum.

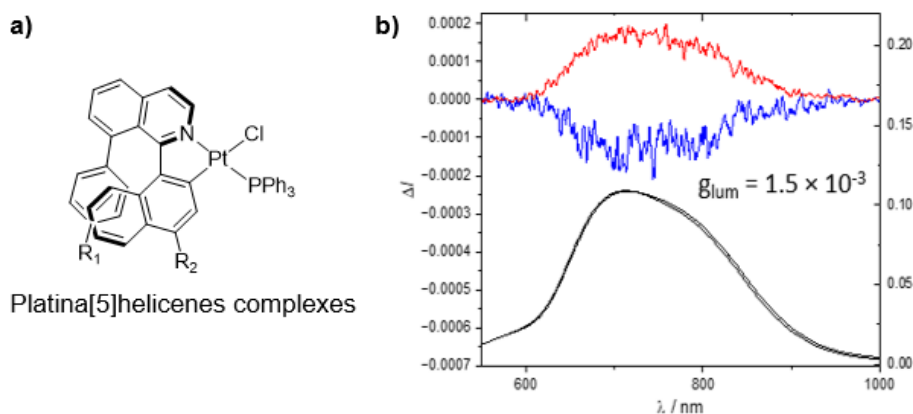


Figure 1: a) General structure of platina[5]helicenes complexes. b) CPL (top) and luminescence (bottom) spectra with dissymmetry factor value for chiral platina[5]helicenes complexes.

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Push-pull photochromic dyes for use in semi-transparent solar cells with dynamic optical properties

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Photochromic solar cells are a new type of photovoltaic device with dynamic optical properties that could potentially be used in glazing and buildings in the future. These solar cells exhibit changes in colour, transparency and photovoltaic performance in response to sunlight conditions.

In 2020, we have shown that the design of push-pull photochromic photosensitizers of the diphenyl-naphthopyran series and their use in a dye-sensitised solar cell configuration is an effective strategy for achieving solar cells with light-driven optical properties. This approach resulted in excellent reversibility of the colouring and decolouring process, as well as efficiencies of the order of 4% for the solar cells. We have also shown that these dyes can be used to fabricate semi-transparent mini-modules with a maximum power output of the order of 35mW. [1]

Recently, we have sought to develop push-pull photochromic dyes with faster bleaching kinetics and better optical properties. In this work, we will outline the synthetic routes used to prepare these photochromic dyes and detail their optoelectronic properties and structure-property relationships [2-3]. In particular, we will show that by appropriate molecular design, it is possible to obtain molecules that exhibit a better photochromic behaviour in devices [4]. We will also present the synthesis and characterisation of new dyes that show a better tuning of their spectra to the photopic response of the human eye allowing producing semi-transparent mini-module with an average visible transmittance varying between 66% and 50% and a colour-rendering index of around 95 in both the uncoloured and coloured states. [5]

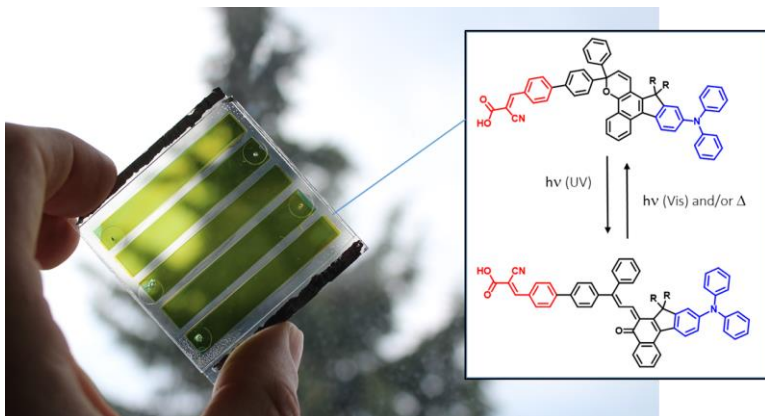


Figure: Image of a semi-transparent mini-module based on a push-pull photochromic dye.

Acknowledgements

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Introducing P in cyanine dyes: smells like polymethine spirit?

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Polymethine cyanines are organic compounds in which a charge (is fully delocalized between two heteroatoms (or heterocycles) over an odd number of sp^2 carbon atoms. Many cyanines have been reported and used for various of applications either in photobiology or in material science.[1] Cyanine dyes have the particularity to have a full charge delocalization on an odd number of C- sp^2 between two lateral nitrogen. This particular structure, called the ideal polymethine state (IPS) leads to characteristic optical properties: ii) a sharp and particularly intense absorption band with a vibronic shoulder at high energy, and (iii) bright luminescence with a very small Stokes shift. Since the 60's, some rare examples of P-containing cyanine dyes [2] were reported but the lack of synthetic access did not allow their democratization like classical cyanine. Furthermore, there are no proofs that an IPS is reached with those structure.

In this work, we will describe our efforts to synthesize different P-containing polymethine cyanines We will also systematically study their structures and optical properties to evaluate if these "phosphacyanines" possess the structural and spectroscopic properties of cyanines in their IPS.[3] And finally, we will attempt to evaluate whether these compounds can, in the future, challenge the 'classical cyanines' in photosciences.

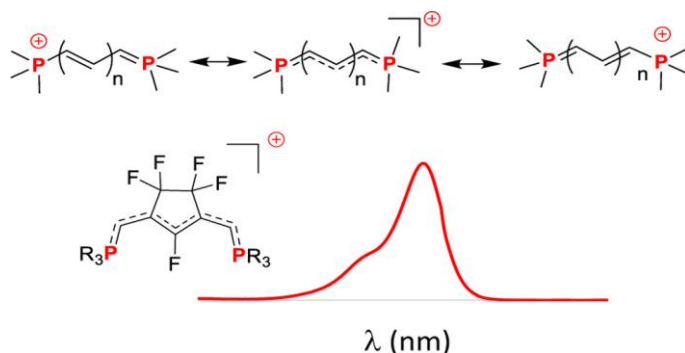


Fig. 1 Phosphacyanines studied here [5]

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Tuning Optoelectronic Properties of Photochromic Dye-sensitized Solar Cells Through Molecular Engineering

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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 use 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.



Acknowledgements

This work was funded under the European Union's Horizon 2020 research and innovation programme (grant agreement number 832606; project PISCO).

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Targeting to improve the efficacy of photodynamic therapy

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Photodynamic therapy (PDT) is part of the therapeutic arsenal for destroying cancer cells. The principle of PDT is to excite a photosensitizing molecule, which activates the oxygen around it to produce reactive oxygen species that destroy tumor cells. To specifically target cancer cells, it is possible to graft vectors that target receptors overexpressed in tumor membranes and/or on neovessels (active targeting) or to use nanoparticles (passive targeting). We will detail these different types of targeting developed in PDT [1,2,3].

There will also be discussion of recent developments in PDT excited by X-rays, where nanoscintillators are used. Specifically, the concept involves using nanoparticles containing a scintillator core that, when excited by X-rays, can emit photons in turn absorbed by the photosensitizer itself grafted into the nanoparticle matrix [4,5].

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Hydrophilic Biocompatible Fluorescent Organic Nanoparticles as Nanocarriers for Biosourced Photosensitizers for Photodynamic Therapy

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The number of people diagnosed with cancer is currently increasing, with almost 20 million new cases and 9.7 million deaths in 2022. The World Health Organisation (OMS) predicts a 77% increase of in the number of people affected by cancer in 2050. Several treatments have been developed to fight this "21st century disease", including surgery, radiotherapy, immunotherapy and chemotherapy. The later approach often causes numerous side effects for the patient. In this context, photodynamic therapy (PDT) has become a highly attractive medical approach for reducing side effects via local activation by light. However, most photosensitizers of interest for PDT are hydrophobic. Porphyrinoids and chlorines, heterocycles - that are good photosensitizers (PSs) generating cytotoxic singlet oxygen under excitation in the presence of O₂ - are an excellent example of insoluble dyes in aqueous medium. To make them dispersible in physiological conditions and improve their bioavailability, pharmacokinetics and preserve their photochemical properties, we selected highly water-soluble and biocompatible fluorescent organic nanoparticles (sFONs) [1] as drug nanocarriers. Soft Fluorescent Organic Nanoparticles (sFONs) made from citric acid and diethyltriamine enriched in free amino groups were used as nanoplatforams for biosourced PSs (i.e., Purpurin 18 (Pp18) and its Chlorin Cp6 derivatives) [2]. The PSs grafting was ensured thanks to both ionic and covalent bonding. The functionalized nanoparticles sFONs-Pp18 retain good water solubility, emit both blue fluorescence when excited in the near UV region and deep-red or NIR fluorescence when excited in the visible absorption bands of the PSs and show high singlet oxygen generation quantum yield in aqueous media (0.72). Moreover, they show high PDT efficiency on colorectal cancer cells (HCT116 and HT-29 cell lines) upon excitation in the deep red (650 nm). As such, these functional organic nanoparticles hold promise both for PDT treatment and theragnostic.

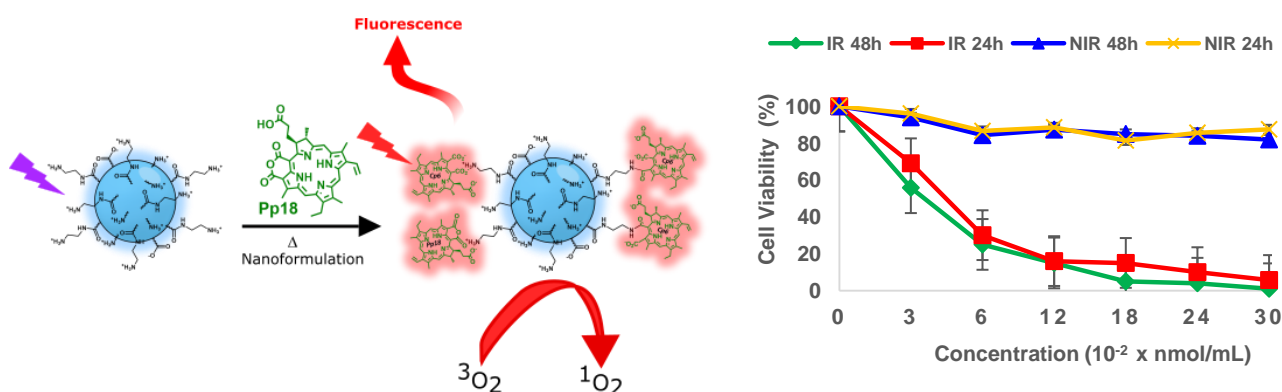


Figure: Nanoformulation of efficient photosensitizer (sFONs-PSs) from biosourced Pp18 and biocompatible Fluorescent Organic Nanoparticles and PDT efficiency on colorectal cancer cells (HCT116).

Acknowledgements

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Light-driven control of G-quadruplex DNA structures with non-covalent azobenzene derivatives

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G-quadruplexes (G4) are non-canonical DNA structures involved in important cell regulatory functions associated with their folding mechanism. Consequently, the design of small ligands capable of modulating their formation/stabilization is of growing interest for the development of new anti-cancer therapies. In particular, the reversible control of G4s using bistable photocommutators offers promising prospects for applications in photopharmacology and DNA nanotechnology, but remains largely unexploited [1]. It has long been demonstrated that the folding/unfolding of human telomeric (HT) G4 sequences can be induced by azobenzene- derived photoswitches such as AZO1 (Fig.1a) [2]. However, dynamics and mechanisms underlying these processes have never been explored. Here, we present a comprehensive study of AZO1 complexes with different G4 sequences by using a combination of steady-state and time-resolved optical and chiroptical spectroscopy. This study revealed a non-cooperative binding mode of AZO1 with a stoichiometry of 8 and 4 respectively with the HT G4 sequences of type 5'-GGG(TTAGGG)3-3' and the thrombin binding aptamer G4 sequence, 5'-GGTTGGTGTGGTTGG-3' (TBA), in the absence of physiological cations. AZO1 binding induces the formation of parallel G4 topologies which can be reversibly unfolded, upon UV- visible excitation, without noticeable fatigue (Fig. 1b). Femtosecond transient absorption measurements showed that AZO1 isomerization is slowed by an order of magnitude when interacting with the G4s (50ps vs. 5ps), while millisecond time-resolved circular dichroism allows to access G4 unfolding, which occurs in ca. 20 ms (Fig. 1c) [3].

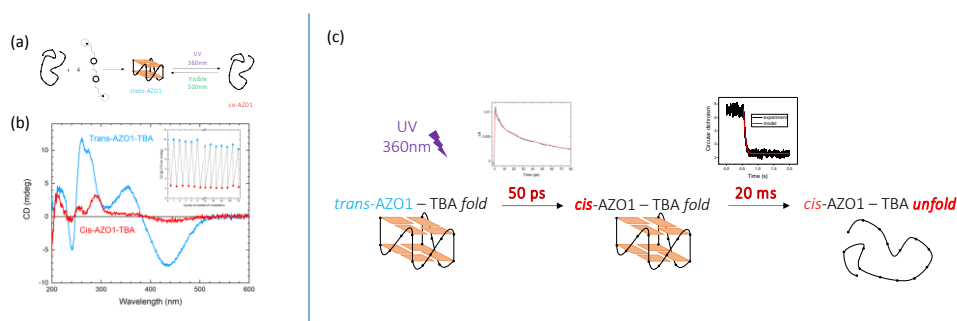


Figure : Photoreversible folding of TBA in 10 mM tris buffer: (a) Schematic representation of the complexation process between AZO1 and TBA (5'-GGTTGGTGTGGTTGG-3'), (b) CD spectra measured after UV (cis-AZO1) and visible (trans-AZO1) irradiations, (c): Unfolding kinetics of TBA upon UV excitation of AZO1 at 360 nm measured with a combination of femtosecond transient absorption and millisecond time-resolved circular dichroism.

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Spatiotemporally controlled Photoaffinity Labelling of nucleic acid secondary structures

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Small synthetic molecules have been shown to be able to bind and stabilize secondary nucleic acid structures known as G-quadruplexes (G4s) *in vitro* and to interfere with biological processes involving genes containing those structures.¹ Together with reversible G4 ligands,² reactive compounds capable of forming covalent bonds with G4s upon thermal, photochemical, target proximity and singlet oxygen activation have been conceived. Photochemical activation strategies exploit a new class of promising G4 ligands with the potential to be harnessed for identification and isolation of G4s.³ Differently from thermal activation, photoaffinity labelling of G4 ligands encompasses the potential to obtain spatial and temporal control over the alkylation event, enriching diagnostic and therapeutic strategies. However, to date, only a few examples of alkylating G4 ligands for photolabeling approaches have been reported. Herein, new families of photoactivatable G4 ligands bearing different photoreactive groups (e. g. quinone methide precursors, benzophenones, and alkyl diazirines) are presented. Once the G4 ligand binding affinity and selectivity towards the biological target were evaluated, their photochemical reactivity was characterized. Laser flash photolysis and product distribution analysis allowed characterizing the nature of the reactive intermediates, and biochemical and analytical methods allowed studying the reactivity of these compounds with oligonucleotide sequences used as prototypes of G4 structures.⁴ Among the different compounds, alkyl diazirine G4 ligands displayed the highest G4 selectivity and alkylation yields and benzophenone G4 ligands showed selective reactivity for thymine nucleobases.

Acknowledgements

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Deciphering Real-Time Mitochondrial Dynamics: Impact of Photo-Oxidative Stress on Lipid Membranes.

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We utilized an original Enhanced Speed Structured Illumination Microscopy (Fast-SIM) imaging setup to explore the dynamics of mitochondrial membranes and ultrastructure under photo-oxidative stress induced by Chlorin-e6. Our Fast-SIM system allowed us to observe and quantify distinct remodeling and shortening of the mitochondrial structure after 60 to 80 seconds of irradiation. These changes were accompanied by fusion events of adjacent inner membrane cristae and global swelling of the organelle. Preceding this, a more extensive sequence was characterized by heightened dynamics within the mitochondrial network, including events such as mitochondrial fission, rapid formation of tubular prolongations, and fluctuations in cristae structure. Thus, our Fast-SIM-based approach enabled quantitative and qualitative characterization of successive steps in the photo-induced oxidation process with sufficient spatial and temporal resolution, and our results compellingly demonstrate the value of this approach for enabling non-invasive dynamic studies of fine organelle structure in living cells.

QUANTUM-DOT BASED NANOSENSORS TO STUDY FOCAL ADHESION ASSEMBLY AND MECHANOSENSING

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Transmission of force between the cell and its environment is essential for the cell to properly accomplish adhesion and migration processes required for tissue building and repair. Transmission of force across the cell membrane is facilitated by focal adhesions (FAs), which are highly organised, self-assembled microstructures[1]. The mechanosensors that make up FAs are specialised proteins sensing cytoskeletal tension. The protein Talin is largely responsible for the mechanosensing of FA. Filamentous actin binds to Talin and with myosin exerts a pulling force[2]. However, the mechanism of mechanosensing still requires more in-depth observation and due to lack of tools, how cells sense the force of the cytoskeleton remains unclear. To improve our comprehension of how Talin interacts with the membrane and its stretching, we have developed intra and inter molecular biosensors. The Förster Resonance Energy Transfer (FRET) nanosensor is composed of Quantum Dot (QD) donor and a dye acceptor, with an ability to measure distances greater than those achievable using conventional FRET. Giant Unilamellar Vesicles (GUVs) were used to understand the adhesion machinery assembly and mechanosensing mechanism. Indeed, reconstituted in vitro systems enable to quantify individual interactions in a highly controlled environment. The entire system allowed to measure distances between the membrane and membrane-recruited Talin. Different lengths of Talin variants have been measured with spectroscopy and microscopy (Fig. A, B). To mimic the cytoskeleton tensile force, Actin and Myosin II (Two major microfilament components) have been used to extend Talin. The mechanosensing process happens when actin filaments contract and Talin stretches upon myosin addition (Fig. C). As a result, Talin changes conformation and enables distance variation measure with an accuracy of <1nm with FRET.

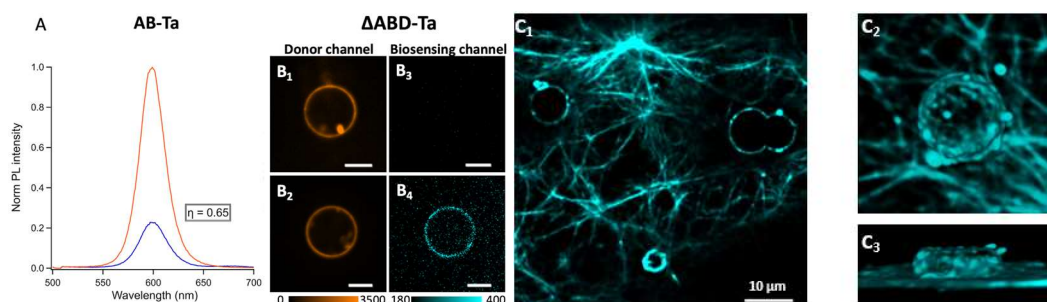


Figure. A) Talin-membrane interaction revealed using fluorescence spectroscopy. Normalized emission spectra of AB-Ta. (N=4). B) Talin-membrane interaction revealed using fluorescence microscopy. Fluorescence images of Δ ABD-Ta. In the donor channel (donor excitation; donor emission) PL intensity of the QD donor before (B₁) and after addition of the acceptor (B₂) and in biosensing channel (donor excitation; acceptor emission) or donor alone (B₃) and donor+acceptor (B₄) Scale bars= 5 μ m. Talin mechanosensing. Talin AB-Ta stretched by actin-myosin. C1) Z slice of an area of few GUVs. C2) 3D Visualization of Actin-Myosin recruitment on GUV with Talin (top view) and C3) lateral view.

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Förster Resonance Energy Transfer combined with Fluorescence Lifetime Imaging: a winning combination for exploring membrane contacts *in cellulo*

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Förster resonance energy transfer (FRET) is a photophysical phenomenon between two chromophores, whose efficiency depends on geometric criteria, particularly the distance between the donor of energy and its acceptor. FRET can be used as a molecular ruler to evaluate the organization or the topology of macromolecules fused to a FRET pair in a biological context (Figure). In this work, the chromophores are fluorescent proteins from the GFP family and the FRET phenomenon is detected through the variations in the donor fluorescence lifetime in imaging mode (FLIM) in the presence of varying amounts of acceptor.

We applied this FRET-FLIM strategy to the analysis of membrane contact sites (MCS) in living cells. These sites are where the membranes of two organelles come in close apposition (Figure). The junction size ranges from 5 nm to 20 nm, a distance that can be probed by FRET. The study of membrane contact sites raises novel biological questions as they are hotspots in the cell that play a pivotal role in the regulation of calcium concentrations and lipid homeostasis. This approach is completely novel in the field and will ultimately enable a dynamic study of the MCS impossible with current methods mainly based on electron microscopy.

In a first step, I will explain how we used our strategy to explore the lateral oligomerization of six proteins involved in the contact sites between the endoplasmic reticulum and the plasma membrane (Figure, left). Our method allowed us to identify the interactions pairwise and explore their stoichiometry, as well as changes in oligomerization levels after mutations of the proteins. In a second step, I will show our first results on the tracking of the MCSs between the endoplasmic reticulum and the plasma membrane using proteins anchored in both membranes with a subcellular resolution.

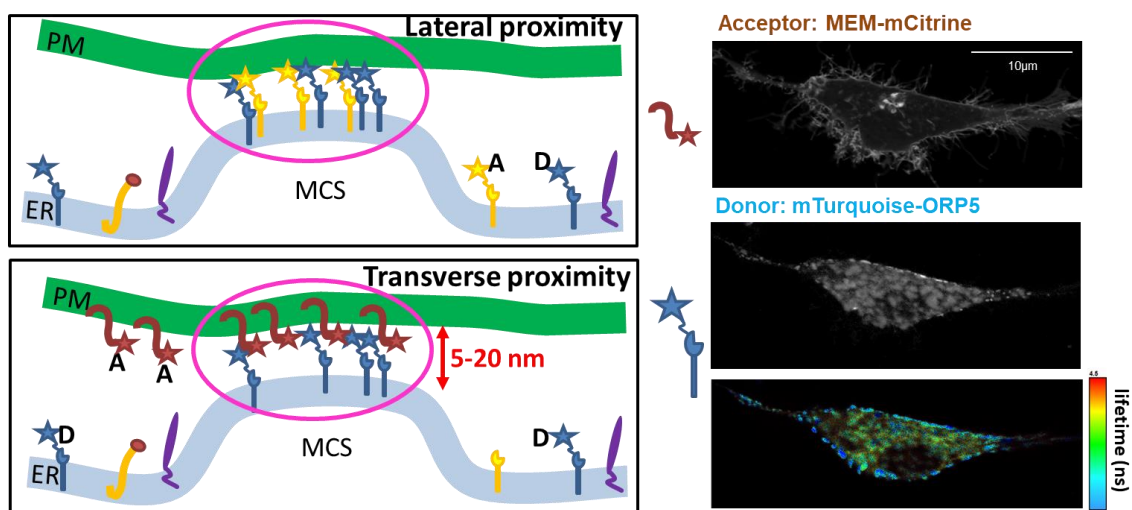


Figure : (Left) Donor and acceptors are fluorescent proteins fused to proteins of the plasma membrane (PM, green) and the endoplasmic reticulum (ER, blue). FRET is only observed when the distance between the donor and acceptor is below 10 nm (pink circle). (Right) Intensity images of a cell expressing the acceptor, a fluorescent protein anchored in the plasma membrane (MEM-mCitrine) and the donor fused to a ER protein, mTurquoise-ORP5. The FLIM image of the donor shows the MCS as blue pixels where the lifetime is reduced.

USING VISIBLE LIGHT FOR BACTERIAL DECONTAMINATION OF BIO-BASED MATERIALS

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Natural molecules were used in this study ¹ to develop a new antibacterial material. Alizarin, a natural dye extracted from madder roots, was modified to graft reactive epoxy functions. This modified epoxy derivative of alizarin has a dual role: as a photosensitizer to initiate polymerization under visible light, and as a monomer due to its reactive epoxy groups. The grafting of epoxy functions allowed covalent integration of the molecule into the polymer network during cationic photopolymerization, preventing dye release. Additionally, mono- and di-epoxy derivatives of eugenol, a natural compound found in cloves known for its antibacterial properties, were used as monomers. Under visible light exposure, the new developed alizarin-derived photosensitizer exhibited good initiation of photopolymerization. Photochemistry played a major role in this project, allowing both material synthesis and bacterial decontamination of its surfaces. Indeed, irradiation of the alizarin derivative led to the generation of reactive oxygen species, including singlet oxygen, renowned for its biocidal properties

Known for its antibacterial properties, the integration of mono- and di-epoxidized eugenol derivatives already gives the material good biocide properties. Visible irradiation of the material enabled complete surface decontamination. 100% efficacy of bacterial decontamination was observed after visible irradiation in the presence of two bacterial strains: *Staphylococcus aureus* and *Escherichia coli*. A material combining the antibacterial properties of eugenol with the photoactivatable properties of alizarin was therefore developed in this project.

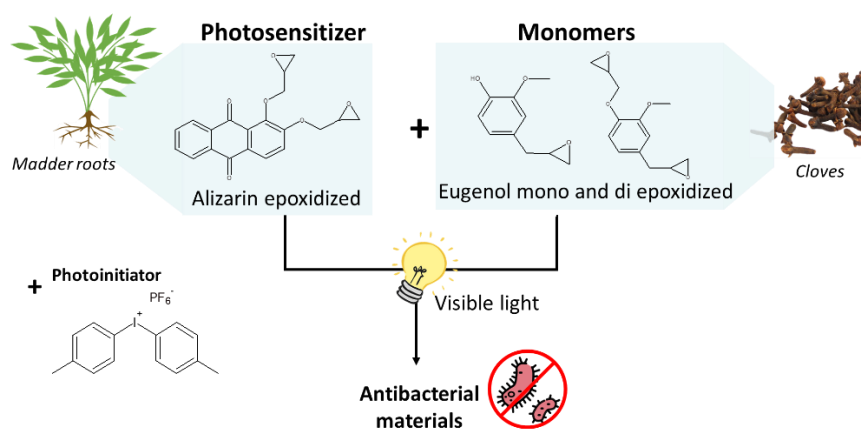


Figure. Photoinduced synthesis of antibacterial and biobased materials from alizarin and eugenol derivatives by visible light irradiation.

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INNOVATIVE PHOTOSENSITIZERS FOR SUSTAINABLY ENGINEERED POLYMERS WITH ADVANCED ANTIBACTERIAL PROPERTIES

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Abstract

Photopolymerization emerges as a cutting-edge chemical synthesis technology, facilitating the creation of polymers through light exposure. This method stands out for its significant contribution to sustainable development, eliminating the need for solvents and offering superior speed compared to conventional thermal polymerization processes. This research delves into the use of innovative porphyrin derivatives for the photopolymerization of bio-acrylates. Porphyrins, known for their exceptional photosensitive properties, are exploited here as photopolymerization initiators. The introduction of two new porphyrin derivatives, developed from polyoxometalates, allowed for a detailed exploration of their photochemical capabilities through fluorescence, photolysis, and time-resolved infrared spectroscopy methods. Their performance as initiators was demonstrated by remarkable initiation efficiency during the radical polymerization of bio-acrylates under 405 nm LED irradiation. The significant advances of this research are also marked by the exceptional results of antibacterial tests. The materials obtained through this photopolymerization method, incorporating specific photosensitizers, revealed superior antibacterial properties. These properties result from the interaction of the incorporated porphyrins with atmospheric oxygen, producing reactive oxygen species capable of efficiently eliminating bacteria. This characteristic opens new perspectives for the use of these polymeric materials in preventing nosocomial infections, offering a potentially revolutionary solution to antibiotic resistance. These discoveries position the photopolymerization of porphyrin derivatives as a promising material synthesis technology for innovative biomedical applications, marking a major advancement in the field of material engineering and public.

Keywords: Photopolymerization; Bio-acrylates; Porphyrin derivatives; Biosourced material.

Thursday May 23 2024

Laser-induced transformation mechanisms of plasmonic Ag nanoparticles in TiO₂ and applications

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Laser processing provides significant advantages in manipulating the colors of plasmonic metasurfaces over large areas. This adaptable and cost-effective method enables the production of high-resolution color images that are visible to the naked eye. Despite inhomogeneity in the size and organization of the metallic nano-objects created through laser processing, the resulting colors are reproducible. This presentation explores the diverse physical and chemical mechanisms induced by lasers on plasmonic metasurfaces composed of silver nanoparticles embedded in a TiO₂ thin film. Under continuous wave (cw)¹, nanosecond, or femtosecond² laser exposure, silver nanoparticles undergo reshaping, shrinking, or growth, and self-organize along subwavelength gratings. Various laser-induced self-organized nanostructures are identified and their origins are elucidated through multi-physical models. Once formed, these self-organized nanostructures exhibit intriguing dichroic optical properties, whose origin, elucidated through electromagnetic modeling, lies in the hybridization of resonant modes.³ These singular optical properties present opportunities for innovation, particularly in high-end anti-counterfeiting applications.⁴ Laser-induced printed image multiplexing emerges as a recently developed inkless technique, providing high flexibility to print multiplexed colored images observable independently under natural light by altering the viewing angle.

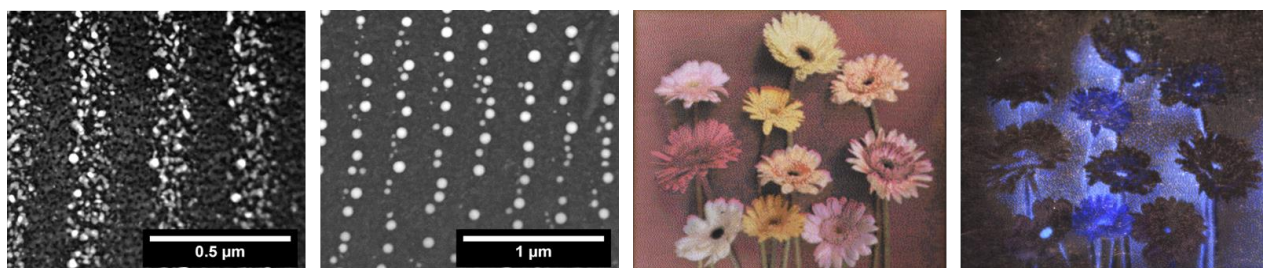


Figure: Laser-processed thin TiO₂ films including Ag nanoparticles. Two left images: transmission electron microscopy images of laser-induced self-organized gratings. Two right images: photographs of a laser-processed film deposited on glass, observed in back-side reflection and in diffraction modes.

Acknowledgements

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Integration of sol-gel TiO₂ thin film on gold nanoparticles for heterogeneous plasmonic photocatalysis

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A novel, straightforward method for fabricating substrates tailored for photocatalysis applications under visible light is introduced. This method involves creating a dense array of gold nanoparticles (AuNPs) through thermal dewetting of a thin gold film, followed by spin-coating of a thin TiO₂ film prepared via sol-gel chemistry. The photocatalytic properties of these nanocomposite films are investigated using surface-enhanced Raman spectroscopy (SERS), focusing on the N-demethylation reaction of methylene blue as a model reaction. This approach reveals that the semiconductor layer on the AuNPs can significantly enhance the efficiency of the photo-induced reaction. Additionally, the SERS analysis demonstrates the impact of parameters such as TiO₂ thickness and position (above or below the AuNPs). Overall, this study highlights that the main mechanism driving the N-demethylation reaction involves both an increase in extinction and enhanced electron transfer facilitated by the semiconductor layer. Furthermore, it dismisses the notion of relying solely on photothermal effects.

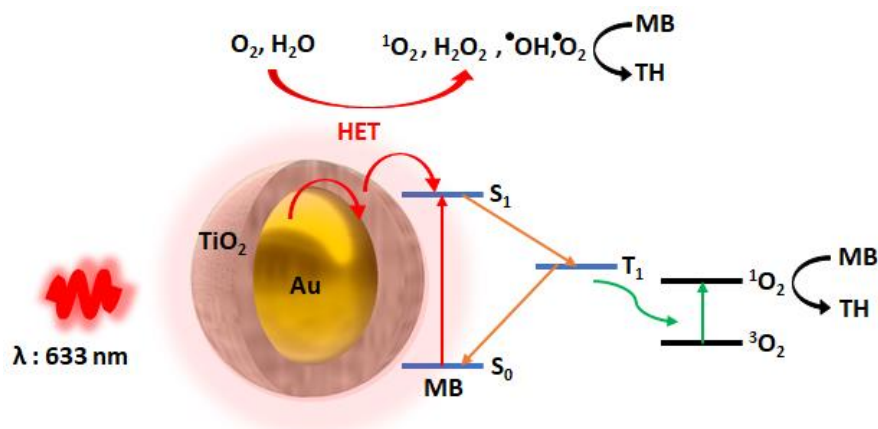


Figure 1. N-demethylation of blue methylene by heterogeneous photocatalysis.

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Polymerization induced through the heat generation of gold nanoparticles under pulsed and continuous laser illumination

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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 emitted light, hot charge carriers and heat. While the photochemical pathway is well known for generating hybrid NPs,[1] thermoplasmonic effects have not been used in this context.

Here, we investigated thermoplasmonic route to graft polymer onto gold NPs. First, we developed a thermopolymer with a threshold temperature around 130°C. Then different parameters were considered to address specifically thermopolymerization through the plasmonic excitation of NPs such as the NPs resonances, laser power and regime. A 532 nm laser illumination was used to match the gold NPs plasmonic resonance. Overall, to generate thermopolymerization through thermoplasmonic effect, high irradiation condition is required. Moreover, we observed thermopolymerization in continuous laser and fs-laser regime with different grafting features (**Figure 1**).

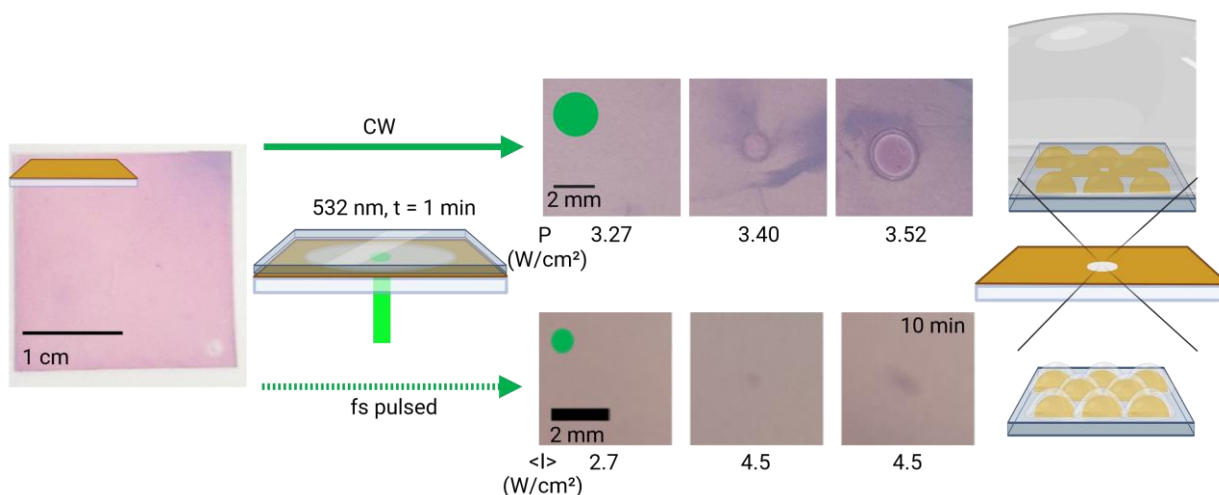


Figure 1: Thermoplasmonic polymerization on gold NPs samples before and after illumination with a continuous laser (top) and with a fs-pulsed laser (bottom). Polymer (dark spot) is observed from 3.40 W/cm² and 4.5 W/cm² respectively.

In continuous laser illumination, a 100- μ m thick polymer dot is observed. Its size might be surprising in comparison with the nanometric size of the NPs. This observation can be explained by a collective heating effect.[2] By comparison, in the fs pulsed laser illumination, a nanometric polymer is generated only around each NPs. In conclusion, by addressing the laser regime in a specific way, it is possible to generate nanometric to millimetric polymer through thermoplasmonics.

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Etude spectroscopique de la perméabilité en phase liquide du polyéthylène au cours de son photovieillissement

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Sous l'effet de facteurs environnementaux tels que la chaleur, la lumière ou encore l'humidité, les polymères vieillissent, ce qui se traduit par une modification irréversible de leurs propriétés d'usage. L'évolution des propriétés mécaniques et optiques des polymères au cours de leur vieillissement a été abondamment étudiée dans la littérature [1]. En contraste, l'effet du vieillissement sur les propriétés barrière des polymères n'a été que très peu abordé, en dépit de l'importance de celles-ci dans de nombreuses applications (emballage, membranes...) [2].

Cette étude vise à corrélérer les modifications de la perméabilité en phase liquide de films de polyéthylène aux changements résultant d'un photovieillissement oxydatif accéléré sur sa structure chimique et son architecture macromoléculaire. Afin d'étudier ces phénomènes, un dispositif expérimental a été spécialement conçu afin de détecter le passage de perméants de structure chimique et de géométrie proches mais de polarité différente. Ce système repose sur une détection in situ et en fonction du temps par spectroscopie de fluorescence et/ou UV-visible.

Cette communication a pour vocation de présenter le développement de ce système et les résultats qui en sont issus (taux de transmission des perméants, *time-lag*...). Ces derniers seront mis en lien avec l'analyse multi-échelle mise en place pour caractériser les conséquences du photovieillissement sur le polyéthylène. Il a ainsi été observé que la polarité du perméant a une influence forte sur sa capacité à perméer et l'évolution de celle-ci durant le vieillissement [3].

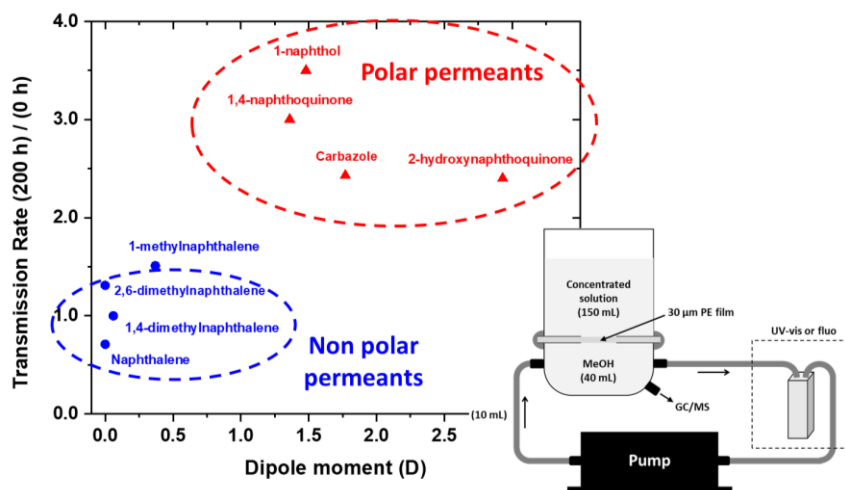


Figure 1 : Rapport du taux de transmission après/avant photovieillissement en fonction du moment dipolaire du perméant et représentation schématique du dispositif expérimental développé.

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Never green enough. Photosynthesis from the planetary to the nanometric scale.

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The universe is a pretty big place. If it's just us, it seems like an awful waste of space¹. And if we are not alone, what would be the common trait among inhabited planets? Most likely, it would be the natural energy sources available, such as the energy generated by thermonuclear reactions occurring in stars, and consequently, the natural energy conversion systems they possess. On our planet, photosynthetic organisms are the primary energy converters that sustain life on Earth for at least three billion years. The chances that this paramount process is general across the universe are very high.

How invaluable and universally relevant would it be to unlock and leverage the capabilities of photosynthetic organisms to set forth a positive and virtuous path? In this presentation, we will embark on a brief journey exploring the profound impacts that technologies based on photosynthesis, including artificial and semi-artificial methods, have already brought or are poised to bring to our planet². Given our urgent need for sustainable and circular processes, these advancements hold great promise for future development.

¹ Carl Sagan, Contact. Simon and Schuster. 1985

² Massimo Trotta. The power of Trees, how photosynthesis helps the planet. Dedalo edizioni. 2022

Ru tris-diphenylsulfonate-phenanthroline is a good challenger to the [Ru(bpy)₃]²⁺ sensitizer with for light-driven H₂ evolution in water

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The tris-bipyridine ruthenium complex, [Ru(bpy)₃]²⁺ (**Rubpy**; Fig. 1), and its derivatives have been widely used for decades as molecular photosensitizers (PSs) associated with a molecular catalyst (Cat) and a sacrificial electron donor (SD), for the photocatalytic reduction of protons to H₂ using visible light energy.^[1] However, the main drawback of this photosensitizer family is the poor stability of its oxidized and reduced forms, especially in water that causes relatively fast deactivation of the photocatalytic systems.

In this context, we were able to improve the stability and efficiency of a Ru based photocatalytic system for hydrogen production in water by using the water-soluble Ru tris-diphenylsulfonate-phenanthroline derivative, Na₄[Ru((SO₃Ph)₂phen)₃] (**RuSPhphen**; Fig. 1) in place of the regular PS, **Rubpy**.^[2] **RuSPhphen** exhibits an absorption coefficient twice as high compared **Rubpy** and much longer lifetime of its excited-state, while keeping almost similar redox potentials, which favors efficient electron transfers between the three components of the system. Moreover, the groups of Castellano^[3a] and Brewer^[3b] have observed high photocatalytic activities with PS/Cat/DS systems using Ru tris-diphenyl-phenanthroline PSs, these performances having been attributed to the high stability of these PSs under photocatalytic conditions. **RuSPhphen** was thus tested by our group with the cobalt tetraazamacrocyclic complex [Co(CR14)Cl₂]⁺ (**Co**), one of the most efficient H₂ production catalysts in acidic water,^[4] and ascorbate (HA⁻) as SD under visible-light irradiation (Fig. 1). The redox and spectroscopic properties of **RuSPhphen** will also be presented, as well as a

thorough photophysical study with the **RuSPhphen/Co/HA⁻** system, in order to explain its high stability which is related to the good photocatalytic activity of this system.

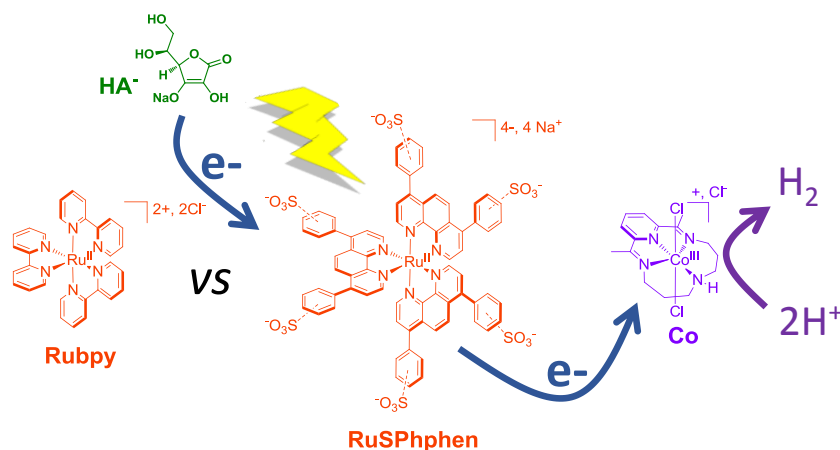


Fig. 1. Photocatalytic systems for H₂ evolution

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Effect of electrolyte additives on the performance of photochromic dye sensitized solar cell

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Photovoltaic energy sources have emerged as a viable alternative to meet the world's growing energy needs. However, today's commercial technologies based on silicon solar cells involve processes that are highly energy intensive, leading to increased values of Energy Payback Time.¹ Among other emerging photovoltaic technologies,² Dye-Sensitized Solar Cells (DSSCs) have shown promising properties given by their ease of fabrication with cheap materials, easy tunability of the absorption properties to obtain solar cells of different colours and high stability.^{3,4}

Given the possibility of working with transparent substrates with DSSCs, the idea of using them as smart windows drove research into dyes with a wide range of colours and on the implementation of photochromic dyes to obtain devices with self-regulating coloration.^{5,6} To this goal, different families of photochromic dyes based on diphenyl-naphthopyran moiety have been intensively studied, with efficiencies above 4% and fast coloration/discoloration kinetics.⁷

The photovoltaic process of DSSCs is generated by a cascade effect of the electrons due to the correct alignment of energy levels in the device architecture. On the other hand, the performance of these solar cells is limited by recombination processes between the different components.

Recent studies showed that the use of electrolyte additives such as Tris(p-methoxyphenyl)amine (TPAA) can provide an intermediate energy level to increase the kinetics of the photovoltaic process (Figure 1), reducing electron recombination and increasing the overall performance.⁸

The main objective of this work is to study new structures sharing the triphenylamine skeleton of TPAA as additives for dye-sensitized solar cells. We will discuss about the synthesis, the characterization and the possible implementation of these molecules in the liquid electrolyte of photochromic dye sensitized solar cells to increase their performances and their stability.

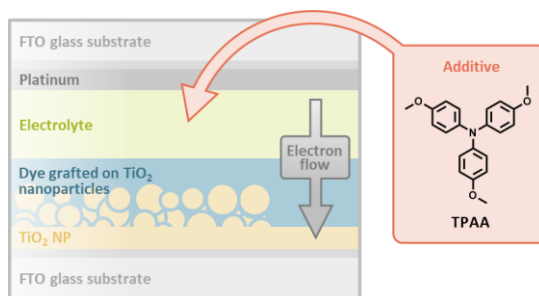


Figure 1 : Schematic view of a DSSC and implementation of TPAA as additive in the electrolyte.

Acknowledgements

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Posters

Self-Assembled Quantum Gold Clusters for Biophotonic Applications

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Gold Quantum Clusters (GQCs) are a class of ultra-small particles presenting tunable photoluminescence (PL) in the first (NIR-I) and second (NIR-II/SWIR) near-infrared windows, making them appealing as tracers for high-resolution imaging of blood vasculature in mice [1-3]. Interestingly, we also noticed a remarkable change in their optical properties with a boost of their absorbance and PL in the NIRs windows when GQCs self-assemble. The main objectives of the SEQUOIA project are now to make the proof of concept that such self-assembly can be obtained and controlled by *in vivo* bio-orthogonal click chemistry after successive intravenous administrations of biocompatible polymer chains and GQCs bearing complementary functions such as strained cyclooctynes (DBCO) and azides. After *in situ* generation, the nano-assemblies will present enhanced biophotonic properties. Thanks to the presence of cRGD-peptide targeting ligands on the polymer, non-invasive diagnostic applications will lead to the sensitive detection of angiogenesis and of a specific biomarker expressed on activated neo-endothelial cells (integrin $\alpha_v\beta_3$).

Controlled formation and the properties of the nano-assemblies will be studied in increasingly complex environments: serum-containing solutions, microfluidic devices, 2D/3D cell culture and then in mice carrying proangiogenic cellulose sponges implanted subcutaneously. All methods are currently available in our laboratories. The versatility and new optical properties of this platform could be exploited for the definition of the next generation of theranostic agents, but also eventually biophotonic sensors and optoelectronic devices.

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LIGHT-DRIVEN CHARGE ACCUMULATION ON RUTHENIUM TRIS-DIIMINE PHOTSENSITIZERS FEATURING FLAVIN-INSPIRED π -EXTENDED LIGANDS

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Photosynthesis is a fascinating source of inspiration to design innovative molecular devices for the conversion and storage of solar energy under a chemical form such as hydrogen or carbon-based fuels. These applications however rely on multielectronic catalytic processes whereas light-driven processes are inherently single-electron events. Nature perfectly overcomes this apparent antagonism thanks to specific cofactors, acting as reversible multielectron relays. Taking inspiration from these systems, an increasing number of sophisticated light-harvesting units, reversibly accumulating multiple redox equivalents upon visible light irradiation, has been studied over the last years.[1] We contributed to the field with the design of mononuclear ruthenium tris-diimine photosensitizers able to reversibly store two electrons coupled to two protons on quinone-inspired π -extended ligands, thus reproducing the mechanism at work with the PSII-plastoquinone couple in the photosynthetic chain.[2] Yet, storing electrons at a sufficiently reducing potential to drive the catalytic processes of interest is a major challenge. We have therefore decided to prepare a new series of complexes incorporating the alloxazine subunit found in natural flavin cofactors, such as FAD (flavin-adenine-dinucleotide) involved in the photosynthetic production of the strong reducing agent NADPH. A spectroscopic and electrochemical investigation of their electronic properties will be presented here in the context of light-driven charge accumulation of multiple reducing equivalents.

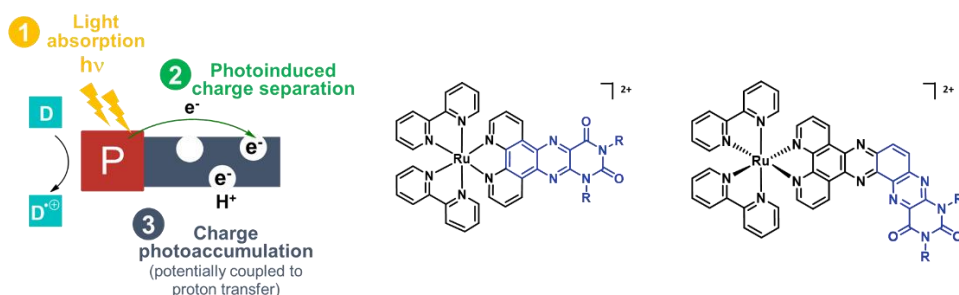


Figure: Schematic representation of the light-driven multiple charge accumulation process and representative structures of ruthenium photosensitizers featuring flavin-inspired π -extended ligands..

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Advancements in Lanthanide Luminescence Sensitization: Leveraging SF and TADF chromophores

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Lanthanide(III) ion-based complexes show a long emission lifetime and sharp emission bands due to their 4f-4f transitions from inner core orbitals¹. These orbitals are weakly influenced by the geometry and environment of the complex, and the nature of their ligands, leading to archetypical emission profiles for each Ln³⁺ ion. One of the main problems in harnessing lanthanide luminescence is the low efficiency of direct excitation. To circumvent this, ligands with desirable absorption properties can be used for a stepwise sensitization. After absorbing a photon, the ligand (antenna) transfers its energy to the metal core inducing the emission of the lanthanide. Increasing the efficiency of this energy transfer is crucial for enhancing luminescence quantum yield and brightness. Overcoming this obstacle requires the design and synthesis of tailored organic antennas.

Herein, we will discuss whether these antennas could exploit photophysical properties such as singlet fission (SF) or thermally activated delayed fluorescence (TADF) processes. On one hand, SF-inducing antennas can convert one absorbed photon into two triplet excitons, theoretically doubling the maximum quantum yield². On the other hand, TADF-based antennas may provide a shorter pseudo-Stokes shift, due to the low gap between singlet and triplet states³, allowing modulation of the excitation wavelength. By selecting antennas with SF or TADF processes, we expect to increase the efficiency of these lanthanide-based systems. The synthesis of the ligands and the photophysical properties of the designed molecules will be presented.

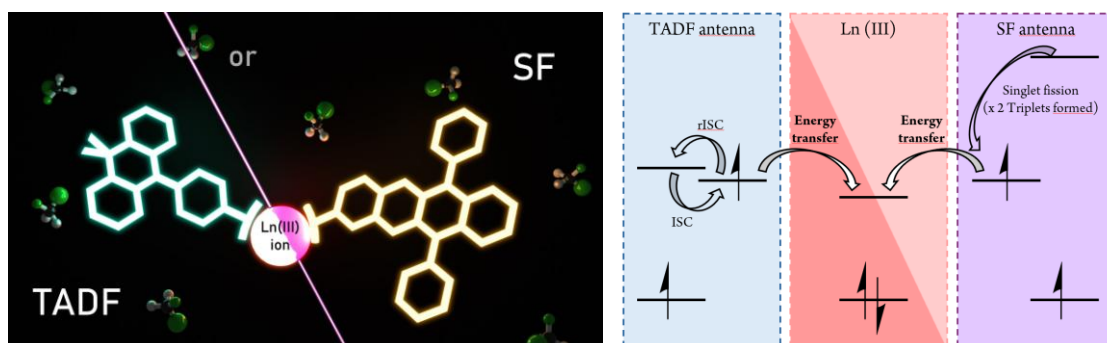


Figure : 3D schematic representation of a lanthanide ion and antennas and a simplified Jablonski-Perrin diagram of the two different cases presented in this work.

Acknowledgements

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HEMIINDIGOS AS ACETYLCHOLINESTERASE INHIBITORS FOR PHOTOPHARMACOLOGICAL APPLICATIONS

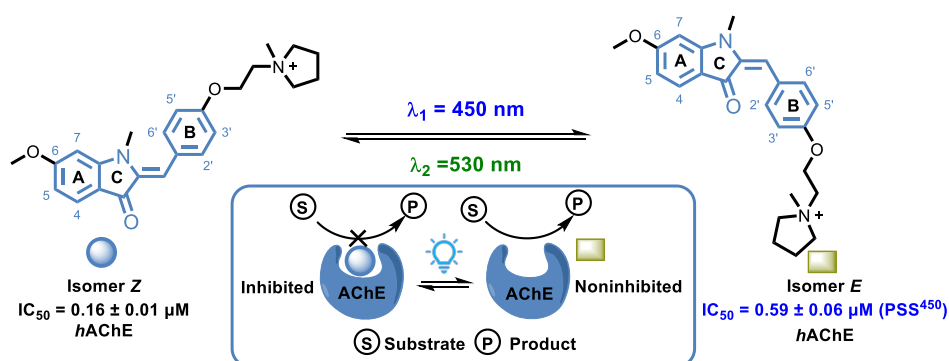
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Hemiindigoids comprise a range of indigo-derived structures mainly represented by aurones, indanones, hemiindigos (HI) and hemithioindigos (HTI). These scaffolds have been associated with many biological activities, such as enzyme inhibition in several models, and studies consecrated to the elucidation of their medicinal potential revealed promising results over the past years. Interestingly, these derivatives possess intrinsic optical properties and in particular, they can have a photochromic behavior, *i.e.* reversible isomerization reactions can be triggered by light illuminations. In particular, when irradiated with light of appropriate wavelength, hemiindigoids can change their molecular geometry from the thermodynamically stable *Z*-isomer to the metastable *E*-isomer¹. Expecting that enzymes will be able to discriminate between the two isomers, this work aims to develop HIs for photopharmacology, a modern branch of pharmacology where light is used as a non-invasive stimulus to control the activity of drugs and, thus, avoid off-target effects. Expecting to obtain a proof-of-concept, we designed and synthesized a series of HIs as acetylcholinesterase (AChE) inhibitors for which the ability to operate as switches in aqueous environment was confirmed. The inhibitory activities over electric eel and human AChE (*ee*AChE and *h*AChE) of the pure *Z*-isomer (dark) and the photostationary state (PSS) equilibrium composition containing both *Z* and *E*-isomers (light) were then evaluated and compared, for which half-maximum inhibitory concentrations (IC_{50}) light/dark ratios reaching up to 3.9 were obtained. We equally performed photochemical/physical characterization for the synthesized HIs and evaluated the effects of structural modifications over these properties. It was observed that *N*-indoxyl methylation produced bathochromic absorption and emission shifts, as well as increased thermal half-lives for the metastable *E*-isomer and higher photoisomerization quantum yields. On the other hand, the introduction of methoxy groups at position 5 of the A-cycle hampered photochromism and fluorescence emission, while producing bathochromic absorption shifts. Finally, for the first time, we obtained a proof-of-concept for the use of HIs in photopharmacology and evaluated the effects of A-cycle functionalization over the photochemical/physical properties of these compounds.



Acknowledgements

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Influence of substituents on the negative photochromic reaction of DASA compounds

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“Negative” photochromic molecules have recently been studied more and more due to their usefulness in various applications (security devices, biological probes or drugs, solar energy storage, etc). [1], [2] Among the negative photochromic families, Donor-Acceptor Stenhouse Adducts (DASA) have gained attention these past few years due to their attractive properties. [3]

In this work, we will present a complete and quantitative spectroscopic study of the photochromic reaction of DASA compounds. Thanks to photokinetic measurements down to the millisecond range, the intermediate folded open-form will be characterized for two different DASA molecules to show the influence of the substituents on their lifetime. [4] Furthermore, fluorescence experiments as a function of irradiation time will complete this study.

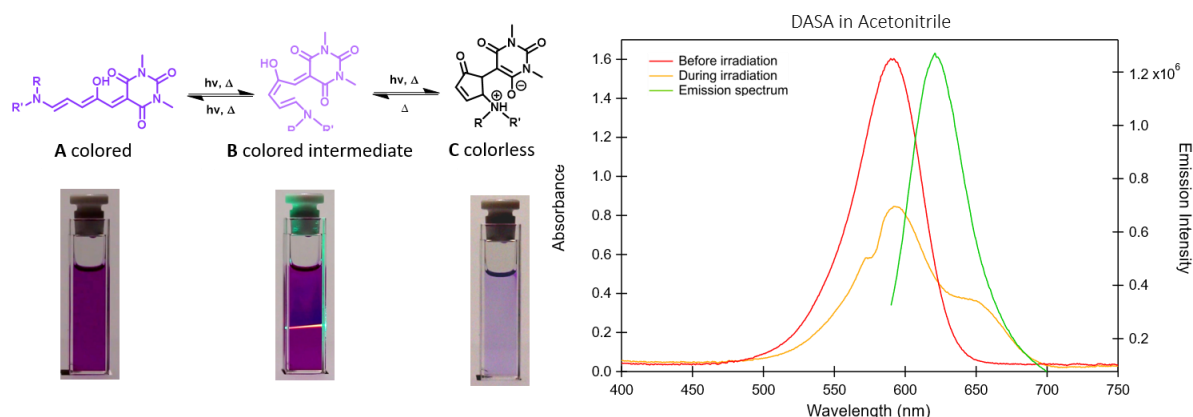


Figure 1. (Left) Photochromic reaction of DASA molecules involving an intermediate folded colored isomer. (Right) Absorption and fluorescence spectra of a typical DASA molecule in acetonitrile, before and during irradiation.

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Photo-assisted recharge of Lithium Ion Battery

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The energy sector in the past years have seen an important change of paradigm, from the coal/oil-based production to a more green and sustainable way. To this day, solar energy is one of the most renewable resources. In this context, our aim is to develop a prototype photo-battery that requires less energy charge compared to a conventional Lithium Ion Battery (LIB). (Fig. 1)

During the charge process of a LIB, the oxidation, occurring at the positive electrode, requires a specific amount of current which depend on the nature of the active materials (AM). The energy supplied by the external circuit can be reduced if the oxidation of the AM is aided by a species with a higher oxidation potential.[1] In this way, and thanks to their photoactivity, semiconductors (SC) are good candidates. They are selected based on their band gap value, their redox potential (under illumination) and their transparency. In this study, we focused on the following materials : ZnO and ITO.

One of the most problem of the SC is their too high oxidation potential (...) compared to the stability of the electrolyte (up to 4.5 V vs Li⁺/Li). To prevent the decomposition of the electrolyte, a protective redox active layer with a middle oxidation potential (...) can be interposed between the SC and the AM, thereby avoiding a direct contact within the electrolyte and the photosensitizer. The protective layer used consists of a coordination complex of Fe(II) (Fig. 2) deposited on the SC *via* an electrochemical technique. Two different methods were used for this purpose.

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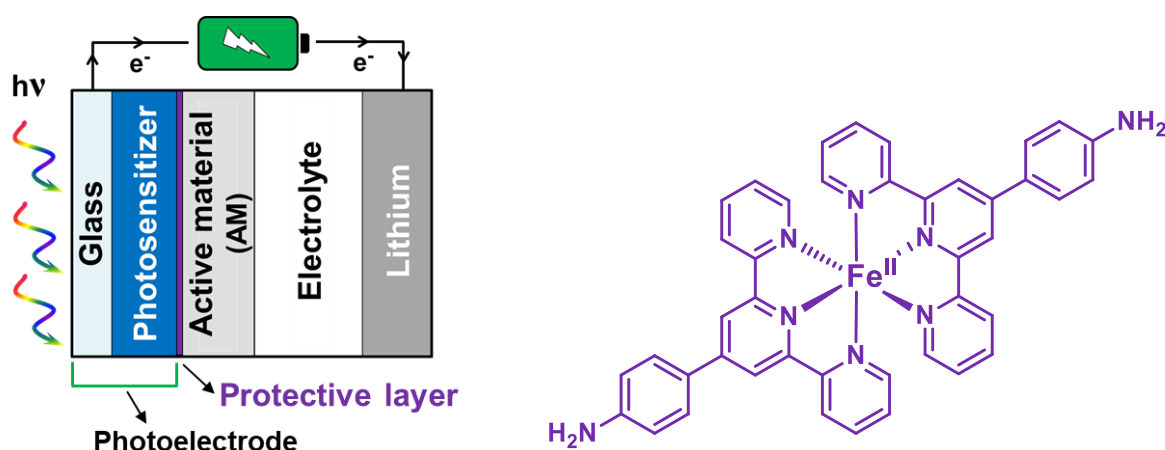


Fig 1. Schematic representation of the proposed photodevice and all the parts that compose the battery. – Fig 2. Starting Fe(II) complex used for the protective layer

MICRO-WAVE ASSISTED SOLVOTHERMAL SYNTHESIS OF LiNbO₃ RARE EARTH DOPED NANOPARTICLES FOR MULTIPHOTONIC BIO-IMAGING

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Lithium niobate, a non-centrosymmetric compound, is widely studied for its many properties (ferroelectricity, piezoelectricity, non-linear optics) [1]. Rare earth doping (to induce photoluminescence properties in the infrared and visible range [2]) and biocompatibility, make LiNbO₃ an ideal candidate as multifunctional nanoparticles (NPs) for biomedical imaging [3]. Advance surface functionalization of those NPs enables cell targeting and imaging by multiphotonic microscopy, *i.e.*, at different emission wavelengths via second harmonic generation (SHG) and up-conversion (UC) generated by infrared excitation in the transparency windows of biological tissues. It has also been shown that SHG emission from LiNbO₃ nanoparticles enables on-demand release of erlotinib-type anti-cancer molecules [4].

As part of the ANR DARE (Deep And REsolved) project, our objective is to carry out an up-scaling of the synthesis of rare earth-doped LiNbO₃ NPs [5]. A sol-gel synthesis step, followed by a microwave-assisted solvothermal treatment, enables the oxide phase to be obtained directly while controlling the morphology of the NPs. The NPs are then characterised by scanning and transmission electron microscopy. The second harmonic generation and photoluminescence properties are characterised by spectroscopy. The changes in the matrix induce by insertion of rare earth ions (by lithium substitution) are also studied. Various solid solutions are also being considered to improve optical properties

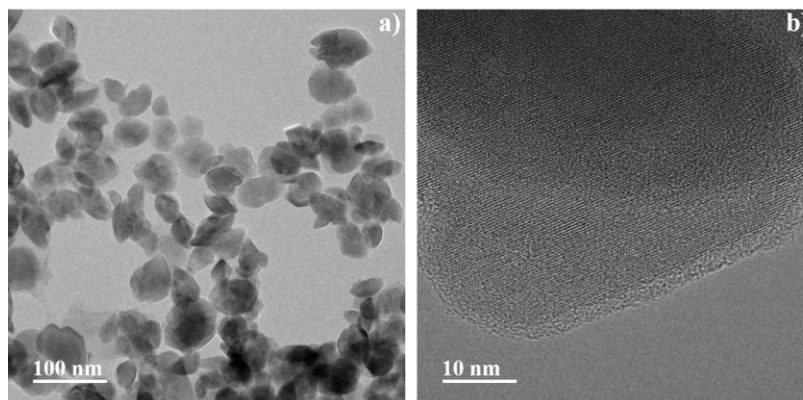


Figure: TEM images of RE:LiNbO₃ NPs obtained by microwave-assisted solvothermal synthesis.

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“IPCMS-ULTRAFAST”: AN OPEN USER FACILITY IN STRASBOURG FUNDED BY PEPR LUMA

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IPCMS is a multidisciplinary research center with international reputation in cutting-edge areas such as spintronics, magnetism, ultrafast condensed matter physics, electron microscopy, STM, biomaterials, synthesis and characterization of functional organic/inorganic materials.

Through the user facility “IPCMS-Ultrafast” (www.pepr-luma.fr/les-plateformes/ipcms/), the Institute offers access to **state-of-the-art ultrafast spectroscopy methods** and advanced equipment for the study of processes such as **spin dynamics in magnetic materials**, and **molecular photoreactivity in solution or in films**. Since March 2024, three installations are open for external users as part of ULTRAFAST LUMA:

- “ATOMAG TMOKE HHG 1kHz” for time-resolved XUV magneto-optical spectroscopy by transverse Kerr effect,
- “UNION TMOKE VIS 10kHz” for visible pump-probe spectroscopy Kerr or Faraday at low temperatures and
- “TRANSIENT ABSORPTION”, UV/VIS/near-IR pump-probe experiment for the study of molecules in solution or films.

The poster will present the technical details and performances of the three set-ups.

External users from French research Institutes and companies can apply for “beam time”: www.pepr-luma.fr/plateformes/deposer-une-demande-dacces/

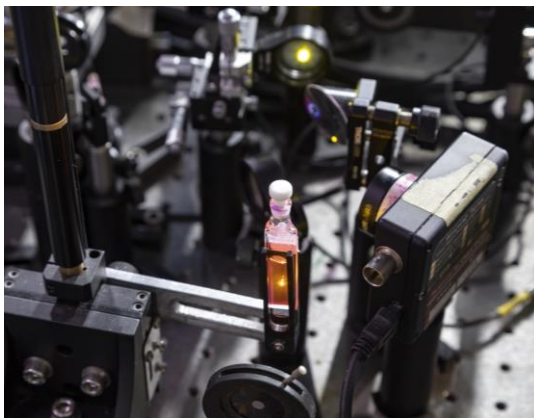


Figure : UV/VIS/near-IR transient absorption with 50 fs resolution: Two femtosecond pump & probe beams cross in a MeOH solution of Rhodamine 6G. The yellow pump and the white-light probe beam are visible on the lens and the parabolic mirror in the background.

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Multi-Perylene Arrays for Photocatalytic Applications

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The development of sustainable strategies for the production of commodity chemicals is a topic of increasing importance. Taken inspiration from nature, and the ability of photosynthetic organisms that are able to efficiently capture and use sunlight to drive multielectronic reactions, the development of molecular photocatalytic systems coupling light-harvesting systems to a desired catalyst is a particularly appealing strategy. The development of efficient antennae able to activate the catalyst under low-light (solar) irradiation remains, however, a great challenge. In this context, the design and implementation of advanced multichromophoric photosensitizers can offer new avenues. In this work, we will present our efforts toward designing multi-perylene arrays, based on a rigid triptycene scaffold and their coupling to well-established Ru-based catalysts known to promote 2-electron alcohols oxidation. The choice of the perylene cores was driven by their exceptional (photo)chemical stability, their good absorption properties in the visible range of the solar spectrum as well as their tuneable redox properties. The triptycene scaffold provides a highly modular platform to organize 1 to 3 perylene moieties around the catalytic center. Finally, the use of Ru-polypyridyl catalysts provide robust systems with well-established reactivity as ideal models to investigate advanced photosensitizer designs for multi-electron reactions. In this poster, we will present the synthesis of various antenna architectures as well as our first attempts to graft these multi-perylene arrays onto an archetypal Ru-polypyridyl core (Figure 1). Preliminary photocatalytic tests for alcohol oxidation will be briefly discussed.

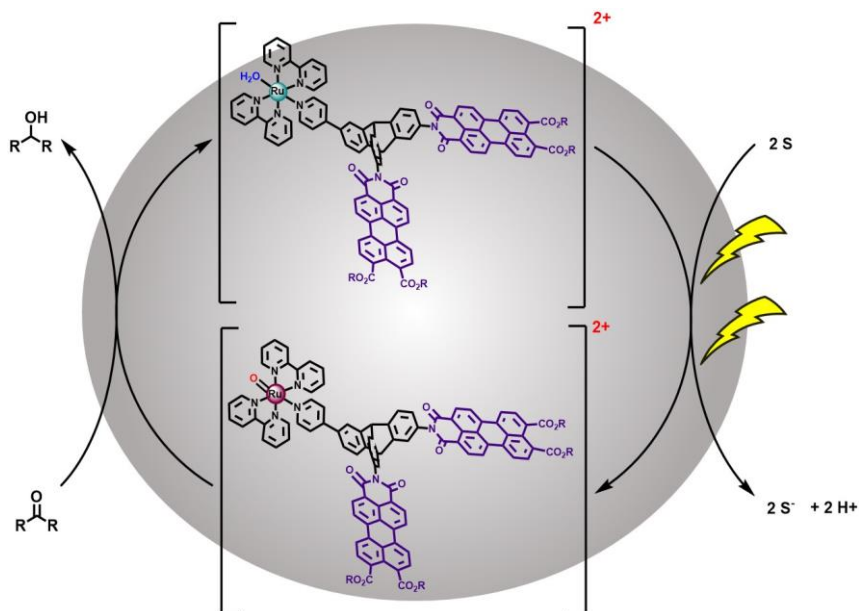


Figure : Ru-polypyridyl/antenna assemblies targeted in this work.

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