Société Chimique de France

SP2P

Société Française
de Physique

Journées Annuelles SP2P

Edition 2021

Subdivision Photochimie, Photophysique, Photosciences

Division Chimie-Physique (DCP)

Société Chimique de France (SCF) / Société Française de Physique (SFP)

INSTITUT DES SCIENCES CHIMIQUES DE RENNES (ISCR)

22 et 23 novembre 2021

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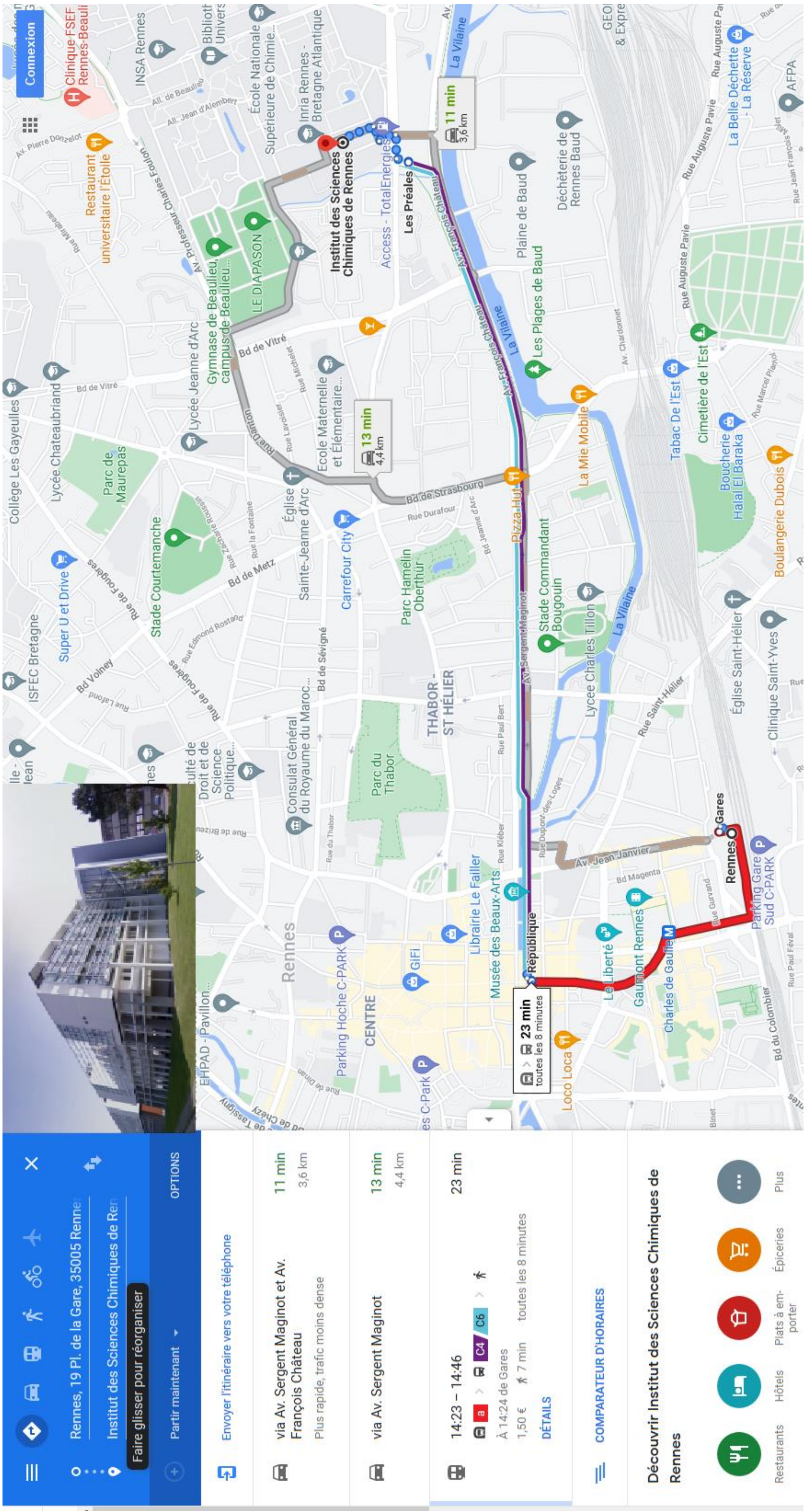

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- Campanile Rennes Atalante (almost on the campus)
- IBIS Rennes Beaulieu (3 min by bus : 3 stops)

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- Atlantic Hôtel Rennes Centre Gare
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Plan du campus Beaulieu

Les journées SP2P’21 se tiendront dans l’amphithéâtre Daniel Grandjean, à l’ISCR bâtiment 10B.

UNIVERSITÉ DE RENNES 1

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263 avenue du Général Leclerc, 35000 Rennes

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11 abce	IPR - Institut de physique de Rennes
11a	CRMPO - Centre régional de mesures physiques de l'Ouest
11 bcd	IETR - Institut d’électronique et des technologies du numérique
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27	Pôle pédagogique licences, salles d'examen
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29	TP biologie
30	TP physique
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41 41 bis 42	ESIR - École supérieure d'ingénieurs de Rennes, Amphithéâtres M, N, L
43	Locaux des associations étudiantes

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06 et	Département GEII
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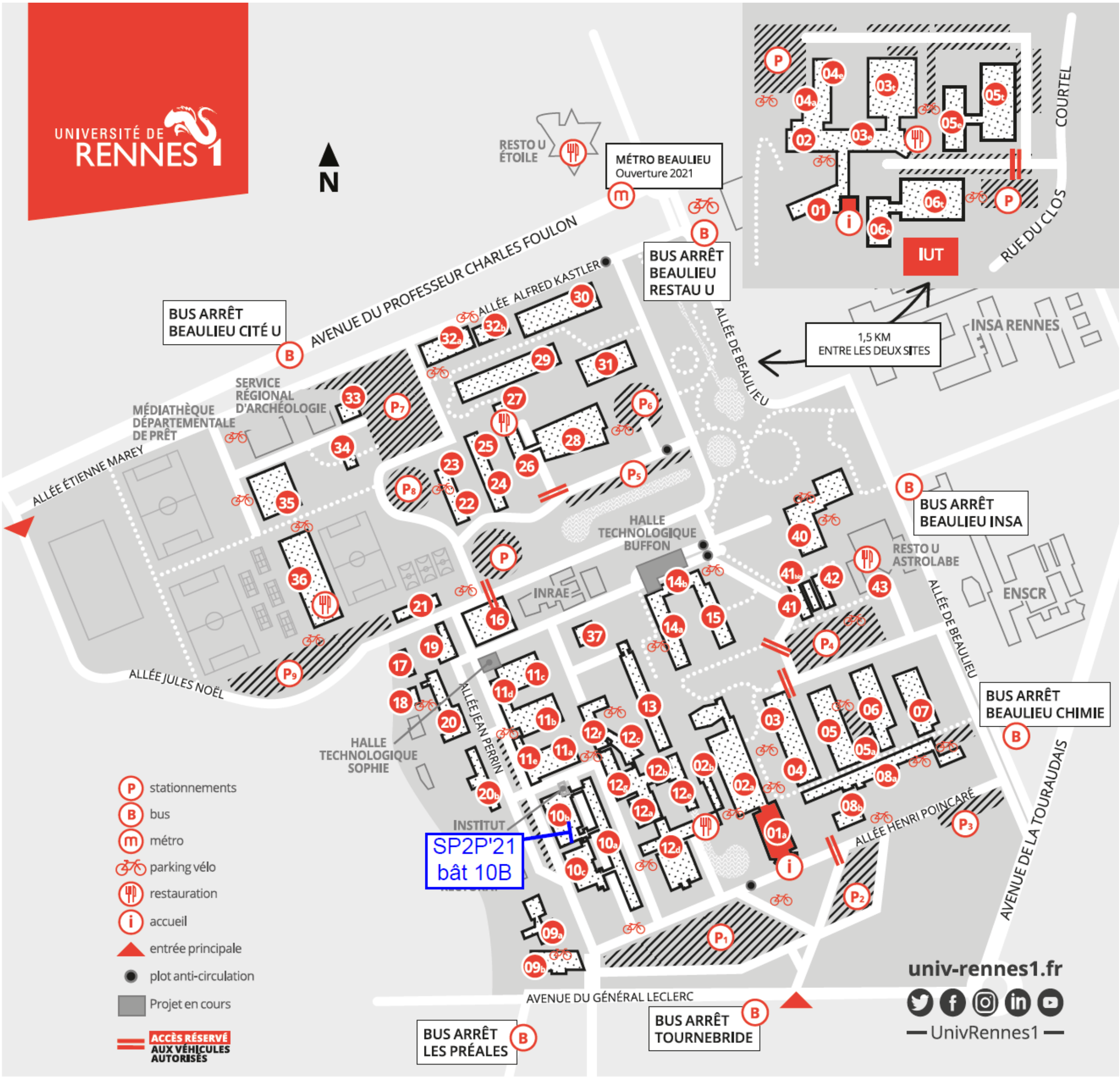

MOTS D'ACCUEIL

C'est avec un plaisir non dissimulé que nous vous accueillons, ces 22-23 novembre 2021 à l'Institut des Sciences Chimiques de Rennes, pour deux journées de conférences autour de la photochimie, de la photophysique et de spectroscopies variées. Il s'agit en effet de notre premier événement post-crise sanitaire sur site, et c'est un grand soulagement de nous retrouver enfin, en chair et en os, pour découvrir (et faire découvrir) les derniers développements scientifiques issus de nos laboratoires. Les années 2020 et 2021 resteront marquées dans l'histoire de notre jeune subdivision comme celles de nos rencontres en visioconférences : *PhotOnline*, organisée par et pour les jeunes chercheurs en octobre 2020, puis le *French Swiss Photochemistry Symposium*, mise en place conjointement avec notre société-sœur la Swiss Photochemistry Section en janvier 2021, furent de francs succès. Mais tout de même, rien ne vaut les envolées au pupitre et au pointeur laser, les discussions pointues devant les posters, ou les débats passionnés aux pauses-café. Profitons bien de ces petits bonheurs, nous avons appris à les savourer...

Les Journées Annuelles 2021 de la Subdivision Photochimie, Photophysique et Photosciences (SP2P), composante de la Division de Chimie Physique, entité de la Société Chimique de France et de la Société Française de Physique, sont traditionnellement l'occasion de donner la voix aux plus jeunes d'entre nous, post-doctorants et doctorants, pour diffuser leurs premiers résultats devant un auditoire exigeant mais bienveillant. C'est aussi la chance de pouvoir écouter des chercheurs confirmés, expérimentateurs ou théoriciens renommés. Nous avons d'ailleurs l'honneur de recevoir pour cette édition 2021 des invités de grande classe : Eric Collet (Keynote, Univ. Rennes), Galina Dubacheva (Univ. Grenobles Alpes), Adèle Laurent (Univ. Nantes) et Gabriel Loget (Univ. Rennes).

Au nom du comité d'organisation de ces Journées, je vous souhaite la bienvenue, et j'espère que vous en profiterez pleinement !

Bien amicalement,

Rémi Métivier, Président de la SP2P

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Julien Boixel, Université de Rennes 1

PROGRAMME SCIENTIFIQUE

Lundi 22 novembre

	13h00	**Accueil** – bâtiment 10B ISCR
	13h30	**Mots d'ouverture – Rémi METIVIER** – Président de la SP2P
Chair – Michel SLIWA	13h40	**Eric COLLET** – *Université de Rennes 1* ***Ultrafast charge transfer and structural dynamics behind photomagnetism***
	14h20	**Galina DUBACHEVA** – *Université Grenoble Alpes* ***Fluorescent nano-switches based on stimuli-responsive supramolecular interactions***
	15h10	Comm. orale 01 – **Patthira SUMSALEE** - *Université de Rennes 1* ***Chiral Luminescence Emitters based on Bicarbazole for Circularly Polarized Organic Emitting Diodes***
	15h30	Comm. orale 02 – **Clément BROUILLAC** - *Université Rennes 1* ***New host materials for high performance single layer phosphorescent light emitting diodes***
	15h50	Pause /posters
Chair – Nathan McClenaghan	16h20	Comm. orale 03 – **Stefan HAACKE** - *Université de Strasbourg* ***Fe(II)-NHC complexes as sustainable photo-sensitizers: What is the nature of the long-lived excited state(s) ?***
	16h40	Comm. orale 04 – **Elise LOGNON** - *Université de Toulouse 3* ***New lights on Dihydropyrene systems photoisomerization process with theoretical study***
	17h00	Comm. orale 05 – **Arnaud FIHEY** - *Université de Rennes 1* ***Quantum description of the photo-induced electron transfer in gold-organic nanomaterials***
	17h20	Comm. orale 06 – **Xingjie FU** - *Université de Lille* ***Influence of temperature on fluorescence and photo-switching quantum yields for photo-switchable fluorescent proteins: the case of rsEGFP2***
	17h40	Comm. orale 07 – **Franck CAMEREL** - *Université de Rennes 1* ***Quantification and applications of the NIR-photothermal properties of nickel-bis(dithiolene) complexes***
	18h00	**Adèle LAURENT** – *Université de Nantes* ***Playing with ESIPT dyes and embedded bilirubine thanks to computationnal tools***
	18h30…	Apéritif – Buffet / posters

PROGRAMME SCIENTIFIQUE

Mardi 23 novembre

	09h00	**Gabriel LOGET** – *Université de Rennes 1* ***Nanostructured Photoelectrodes: From Energy to Luminescence***
Chair – Olivier SOPERA	09h30	Comm. orale 08 – **Nour EL BEYROUTI** - *Université de Rennes 1* ***Ligand-Driven Light switching of Single Molecule Magnets***
	09h50	Comm. orale 09 – **Jonathan LONG** - *ENS Paris-Saclay* ***Modulation of arene-RuII complexes structures and properties with ortho-sulfonamide azobenzene ligands***
	10h10	Comm. orale 10 – **Isabelle NAVIZET** - *Université Gustave Eiffel* ***Modelling absorption and emission spectra taking into account the dynamic environment: example of firefly bioluminescent systems and analogues***
	10h30	Comm. orale 11 – **Yann MOLARD** - *Université de Rennes 1* ***Octahedral Molybdenum clusters containing hybrid materials: from their synthesis to their studies on the Caphter platform***
	10h50	Pause / posters
Chair – Niloufar SHAFIZADEH	11h20	Comm. orale 12 – **Pierre-Antoine BOUIT** - *Université de Rennes 1* ***Fluorescence switching with bisphosphonium***
	11h40	Comm. orale 13 – **Marie BARALE** - *Université de Rennes 1* ***Synthesis and characterization of atropoisomeric pyrene- based dithienylethenes: Optical control of luminescence properties***
	12h00	Comm. orale 14 – **Nicolas FABRE** - *ENS Paris-Saclay* ***Fluorescence photoswitching of diarylethene dyads: from energy transfer to unconventional behavior and photokinetics***
	12h20	Comm. orale 15 – **Yann TROLEZ** - *Université de Rennes 1* ***1,1,4,4-tetracyanobutadienes derived from ynamides: new fluorophores sensitive to their environment***
	12h40	Buffet / posters
Chair – Jérôme CHAUVIN	14h00	Comm. orale 17 – **Louise BRELOY** - *Université Paris-Est Créteil* ***Design of macrocycles as versatile visible-light photoinitiators for bulk free-radical and cationic polymerizations***
	14h20	Comm. orale 18 – **Thibault BARON** - *Université de Nantes* ***Pyrrolopyrrole cyanine dyes as Near InfraRed photosensitizer for hydrogen production via water reduction using Dye Sensitized Photocatalysis system***
	14h40	Comm. orale 19 – **Julien BERTHOMIER** - *Université Paris-Saclay* ***Photo-isomérisation sélective de l'acide salicylique***
	15h00	**Clôture – Rémi METIVIER** – Président de la SP2P

RESUMES

Plénière

et

Invitées

Conférence plénière

Ultrafast charge transfer and structural dynamics behind photomagnetism

E. Collet,[1] **S. Zerdane,[1] G. Azzolina,[1] R. Bertoni,[1] E. Trzop,[1] C. Mariette,[1] M. Cammarata,[1]**
S. Mazerat,[2] L. Catala,[2] T. Mallah,[2] S. F. Matar,[3,4] H. Tokoro,[5] K. Imoto,[6] M. Yoshikiyo,[6] S. Ohkoshi[6]

[1] *Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France*
[2] *ICMMO, Université Paris-Sud, CNRS, Université Paris-Saclay, 91405 Orsay cedex, France*
[3] *ICMCB, CNRS UMR 5026, Université de Bordeaux, F-33600 Pessac, France.*
[4] *Lebanese German University (LGU), Sahel Alma Campus, PO Box 206, Jounieh, Lebanon*
[5] *Department of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Japan*
[6] *Department of Chemistry, School of Science, The University of Tokyo, Tokyo, Japan.*

Email: eric.collet@univ-rennes1.fr

Photoinduced charge-transfer (CT) is an important process in nature and technology, responsible for the emergence of exotic functionalities, like magnetic order for cyanide-bridged bimetallic coordination networks. Despite its broad interest and intensive developments in chemistry and material sciences, the atomic-scale description of the photoinduced process, coupling intermetallic CT and spin-transition, has been debated for decades and was beyond reach due to its extreme speed. We study this process in a prototype cyanide-bridged CoFe system by femtosecond X-ray and optical absorption spectroscopies, allowing for disentangling ultrafast electronic and structural dynamics [1]. Our results demonstrate that it is the spin-transition that occurs first on the Co site within 50 fs, which drives the subsequent Fe-to-Co charge-transfer within 200 fs. In the case of the RbMnFe Prussian blue analogue, we have shown that two photoswitching pathways exist, depending on the excitation pump wavelength, which is confirmed by band structure calculations [2,3].

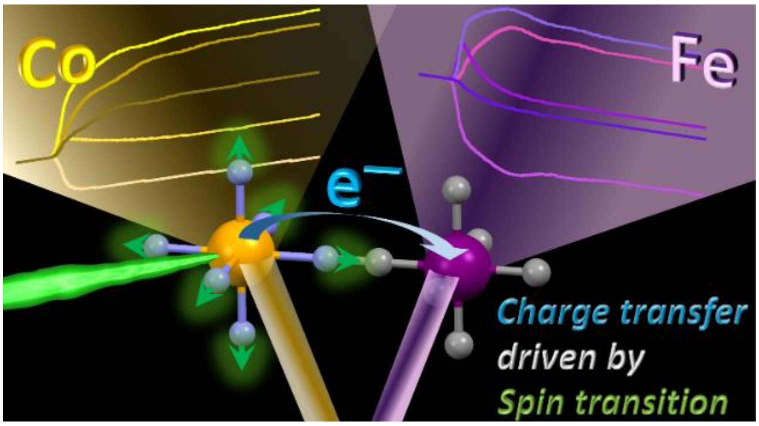

Figure 1. Title of the figure.

[1] M. Cammarata, *Nature Chemistry*, **2021**, 13, 10-14.

[2] G. Azzolina, *Angewandte Chemie I.E.*, **2021**, 60, 23267-23273.

[3] G. Azzolina, *J. Mat. Chel. C*, **2021**, 9, 6773-6780.

Conférence Invitée 1

Fluorescent nano-switches based on stimuli-responsive supramolecular interactions

L. Martin, [a] *D. Kamzabek,* [b] *B. Chabaud,* [a] *F. Sciortino,* [a] *F. Miomandre,* [b] *H. Bonnet,* [a] *L. Guérente,* [a] *D. Boturyn,* [a] *R. Auzély* [c] *and G. V. Dubacheva* [a]

[a]DCM, Univ. Grenoble Alpes; [b]PPSM, ENS Paris-Saclay; [c]CERMAV, Grenoble

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Tuning fluorescence reversibly and in a single nanostructure is of great interest for different applications from bioanalytic nanoprobes to sensors and photo-electronic devices. We propose to use stimuli-responsive supramolecular interactions to design dynamic plasmonic systems allowing one to tune reversibly the nanoparticle/fluorophore distance and thereby the resulting fluorescence (Fig. 1). Our recent results obtained with gold nanoparticles linked with fluorophores through thermoresponsive poly(N-isopropylacrylamide) polymer provide the proof for the proposed approach [1]. We are now extending it to oligo(ethylene glycol) copolymers having tunable transition temperature [2], aiming to produce multifunctional bioanalytical nano-probes, combining the possibility of local heating with nano-scale temperature sensing. In parallel, we develop fluorescence switches based on redox-driven host/guest interactions such as between β-cyclodextrin and its guest ferrocene. Our previous studies on surfaces showed that several levels of control are achievable with host/guest chemistry, including strong binding at high selectivity thanks to multivalency, combined with reversibility under external stimuli [3]. Our goal is to extend this strategy from surfaces to nanostructures by developing redox- or photo-sensitive nano- switches suitable for fluorescence sensing assays in solutions and on surfaces.

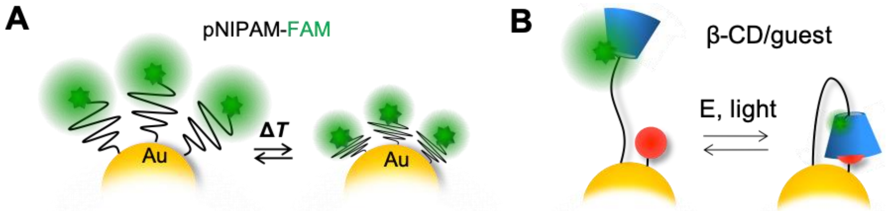


Fig. 1. Fluorescence nano-switches based on thermo-responsive pNIPAM (A) and host/guest interactions sensitive to electrochemical stimuli or light (B).

[1] D. Kamzabek et al, Langmuir, 37, 10971–10978 (2021)

[2] J. Jing et al, J. Mater. Chem. B, 1, 3883–3887 (2013); M. Rippe et al, Biomater. Sci., 7, 2850–2860 (2019)
[3] G. Dubacheva et al., Chem. Commun., 47, 3565-3567 (2011); G. Dubacheva et al., Proc. Natl. Acad. Sci. USA, 112, 5579-5584 (2015)

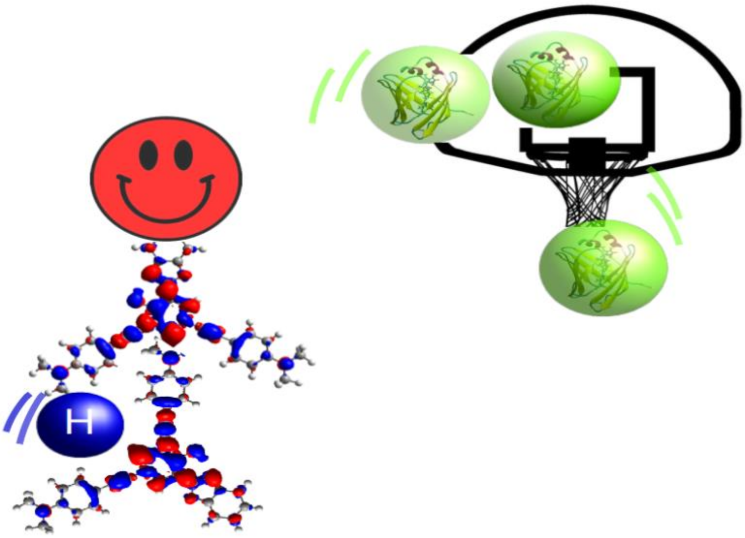
Conférence Invitée 2

Playing with ESIPT dyes and embedded bilirubine thanks to computationnal tools

Adèle D. Laurent[1]

[1] *Laboratoire CEISAM UMR UN-CNRS 6230, Université de Nantes, Nantes F-44000, France*
Email: Adele.Laurent@univ-nantes.fr

Light-sensitive compounds are playing a central role for establishing precise control over the properties and functions of chemical, material and biological systems. In the present talk, I will present two different systems were are dealing with using computational methods, and more particularly Time-Dependent Density Functional Theory (TD-DFT), Molecular Dynamics simulations, and hybrid quantum mechanics and molecular mechanics (QM/MM) methods. Firstly, dyes undergoing excited state intramolecular proton transfer (ESIPT) will be presented showing how theoretical works can help chemists to design new compounds. [1,2] Secondly, the first critical steps towards the understanding of the impact of a single mutation in a protein onto fluorescence intensity will show you how the global structural change tune the optical properties.[3]



[1] Y. Houari, A. Charaf-Eddin, A. D. Laurent, J. Massue, R. Ziessel, G. Ulrich, D. Jacquemin, *Phys. Chem. Chem. Phys.* **2014**, 16, 1319.

[2] Y. Houari, S. Chibani, D. Jacquemin and A. D. Laurent *J. Phys. Chem. B*, **2015,** 119, 2180.
[3] M. Asad and A. D. Laurent, *Phys Chem Chem Phys*, **2021**, submitted.

Conférence Invitée 3

Nanostructured Photoelectrodes: From Energy to Luminescence

Gabriel Loget

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Photoelectrochemistry at semiconductors electrodes is a wide field of research that combines photon absorption and electrochemical charge transfer. The simultaneous occurrence of both these stimuli at the solid/liquid interface allows triggering electrochemical reactions with a considerably lowered energy input. So far, this phenomenon has been proven very promising for solar-to-fuel conversion applications (e.g., water splitting or CO_2 reduction).[1] In this presentation, I will present the recent progress of our group in the fabrication and understanding of inhomogeneously coated Si-based photoanodes.[2] On the other hand, electrochemiluminescence (ECL) is a light-emitting process and a powerful tool in analytical chemistry. This phenomenon is induced by the excited state of a luminophore, which is generated by an electrochemical reaction at an electrode surface.[3] Thus, photoelectrochemistry at semiconductors is a process where an electrode absorbs light, as opposed to ECL, where the electrode can be considered an emitter. We have been recently exploring the combination of these two concepts, which will be presented in the second part of this contribution.[4]

[1] a) K. Sun et al. *Chem. Rev.*, **2014**, 114, 8662. b) S. A. Lee et al. *ACS Material Lett.*, **2020**, 2, 1, 107.

[2] a) K. Oh et al. *Energy Environ. Sci.*, **2018**, 11, 2990. c) G. Loget et al. *Nat. Commun.,* **2019**, 10, 3522. c) K. Oh et al. *Nanoscale,* **2021**,13, 1997.

[3] N. Sojic, Analytical electrogenerated chemiluminescence: from fundamentals to bioassays The Royal Society of Chemistry, **2020.**

[4] a) Y. Zhao et al. *J. Am. Chem. Soc.,* **2019**, 141, 13013. b) J. Yu et al. *Angew. Chem. Int. Ed.,* **2020**, 59, 15157. c) J. Yu et al. *Electrochim. Acta*, **2021**, 381, 138238. d) Y. Zhao et al. *Cell Rep. Phys. Sci.,* in press.

RESUMES

Communications Orales

Communication Orale 01

Chiral Luminescence Emitters based on Bicarbazole for Circularly Polarized Organic Emitting Diodes

Patthira Sumsalee,[1] Laura Abella,[2] Grégory Pieters,[3] Jochen Autschbach[2,*], Jeanne Crassous[1] and Ludovic Favereau[1,*]

[1] Univ Rennes, CNRS, ISCR-UMR 6226, ScanMAT–UMS 2001, F-35000 Rennes, France.

[2] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260, USA.

[3] Université Paris-Saclay, CEA, INRAE, Département Médicaments et Technologies pour la Santé (DMTS), SCBM, 91191 Gif-sur-Yvette, France.

Email: patthira.sumsalee@univ-rennes1.fr

Chiral molecules are capable of emitting spontaneously circularly polarized (CP) light, opposite in sign (either left- or right-CP luminescence, CPL) for the two enantiomers.[1] Such specific feature have made chiral emitters particularly appealing for the development of organic light emitting diodes (OLEDs) with CP electroluminescence (CP-OLEDs), which has recently emerged as an interesting approach to improve displays performances in comparison to currently used unpolarized OLEDs.[2] CP-emitters with thermally activated delayed fluorescence (TADF) have recently attracted significant attention owing to the possibility to simultaneously combine the use of both singlet and triplet excitons conversion for high devices efficiency, and a circularly polarized light emission.[3] In this presentation, I will show our last results regarding the design of chiral TADF emitters based on either a covalent donor-acceptor approach or through the development of luminescent chiral exciplexes (figure 1).

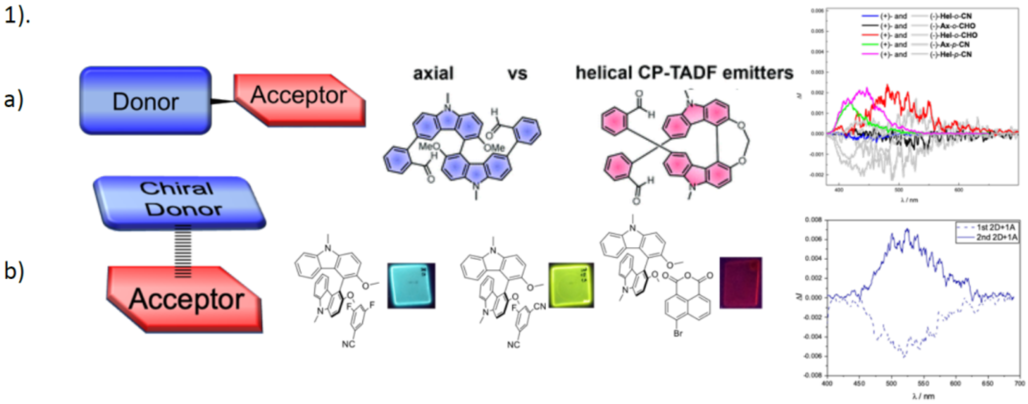

Figure 1. a) Axial and helical bicarbazole donor-acceptor molecular systems and CPL spectra in toluene (M^{-5}) and b) Chiral TADF exciplexes with pictures of their solid-state emissions and CPL spectra of donor and 3-fluorophthalonirile in neat film.

[1] S. Feuillastre, M. Pauton, L. Gao, A. Desmarchelier, A. J. Riives, D. Prim, D. Tondelier, B. Geffroy, G. Muller, G. Clavier, and G. Pieters, *J. Am. Chem. Soc.*, **2016**, 138, 3990-3993.

[2] L. Frederic, A. Desmarchelier, L. Favereau and G. Pieters, *Adv. Funct. Mater.*, **2021**, 31, 2010281.

[3] P. Sumsalee, L. Abella, T. Roisnel, S. Lebrequier, G. Pieters, J. Autschbach, J. Crassous and L. Favereau, *J. Mater. Chem. C*, **2021**, 9, 11905-11914.

[4] a) S. Tan, K. Jinnai, R. Kabe and C. Adachi, *Adv. Mater.* **2021**, 33, 2008844; b) P. Sumsalee, L. Abella, S. Kasemthaveechok, N. Vanthuyne, M. Cordier, G. Pieters, J. Autschbach, J. Crassous and L. Favereau, *Chem. Eur. J.* **2021**, doi.org/10.1002/chem.202102765; c) K. Takaish, S. Murakami, K. Iwachido and T. Ema, *Chem. Sci.*, **2021**, https://doi.org/10.1039/D1SC04403F.

Communication Orale 02

New host materials for high performance single layer phosphorescent light emitting diodes

Clément Brouillac,[1] **Fabien Lucas,**[3] **Emmanuel Jacques,**[2] **Denis Tondelier,**[3] **Cassandre Quinton,**[1]
Joëlle Rault-Berthelot,[1] **Cyril Poriel**[1]

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[b]IETR, Département Microelectronique & Microcapteurs UMR CNRS 6264, F-35000 Rennes, France

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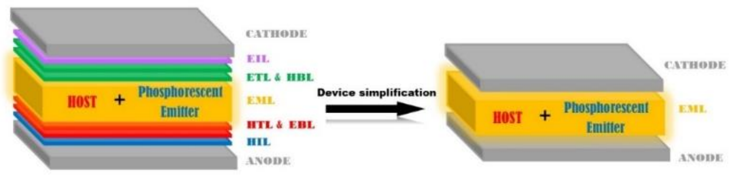
Nowadays, OLEDs (Organic Light-Emitting Diodes) technology is present in everyday life. It is mainly found in smartphone and television screens, but also, more recently, for lighting. Organic electrophosphorescent diodes (PhOLEDs) are the second and most mature generation of OLEDs. In this technology, all the high-efficiency PhOLEDs are multi-layer devices constituted, in addition to the emissive layer (EML), of a stack of functional organic layers. These layers play a crucial role in the device performance as they improve the injection, transport, and recombination of charges within the EML. However, in order to fit with the energetic and ecological transition, PhOLED technology should still be improved. Single-layer PhOLEDs (SL-PhOLEDs) represent ideal OLEDs, consisting only of the electrodes and the EML[1]. Simplifying the multilayers structure is then crucial to reduce the amount of commodities, the manufacture complexity, the production and recycling costs for real-life applications. However, reaching high-performance SL-PhOLED is far from easy, as removing the functional layers of an OLED stack dramatically decreases the performance. To achieve high SL-PhOLED efficiency, the efficient injection, transport, and recombination of charges should be insured by the EML, and particularly, by the host material[2-4]. Herein, two host materials have been investigated. They are constructed on the association of an electron-rich unit (indoloacridine or dihydroquinolinoacridine) connected by a shared spiro carbon atom to an electron-deficient 2,7-bis(diphenylphosphineoxide)-fluorene. In addition to a high E_T value, adequate highest occupied molecular orbital/lowest unoccupied molecular orbital energy levels and important thermal stability, the key point in this molecular design is the suitable balance between hole and electron mobilities, which leads to good performance in a SL-PhOLED.



Multi-layer PhOLED   Single-layer PhOLED

Figure 1. Schematic representation of a multi-layer PhOLED (left) and a single-layer PhOLED (right).

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Communication Orale 03

Fe(II)-NHC complexes as sustainable photo-sensitizers: What is the nature of the long-lived excited state(s) ?

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One recent development in the realm of sustainable, green chemistry is to explore the replacement of rare transition metals like Ir, Pt and Pd in metalorganic complexes by more abundant elements like Fe, Cu or Cr. Coordination of Fe(II) with electron-rich carbene bonds can considerably enhance the ligand field splitting energy (LFSE) and ^{3}MCLT lifetimes, up to ≈2 ns, were reported [1]. Indeed, if the LFSE is high enough, a situation akin to the one in noble metals may be created: Metal-centred (MC) states would be higher in energy than the ^{3}MLCT states, thus preventing ultrafast internal conversion.

Our work addresses the ultrafast photophysics of such Fe(II)-NHC (N-heterocyclic carbene) compounds with four carbene bonds [2]. Here, it appears quickly that the ligand field splitting argument applies only to the energy level ordering in the Franck-Condon region. But, the excited state relaxation involves vibrational dynamics, leading to a possible crossing of MLCT's into metal-centered (MC) potential energy surfaces and a progressive change in the nature of the long-lived excited state. Indeed, it was recently shown that the prototypical $[Fe(bmip)_2]^{2+}$ complex, where bmip= 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine, displays an ultrafast ^{3}MLCT/^{3}MC branching upon relaxation from the optically excited ^{1}MLCT, which potentially limits the benefit of a purely MLCT-driven excited state photo-chemistry (e.g. electron transfer) [3].

The double-carboxylated form of $[Fe(bmip)_2]^{2+}$, termed $[Fe(bmipc)_2]^{2+}$, is a decent photosensitizer, with an 18-20 ps excited state lifetime, recently used in solar cell sensitised by Fe(II) complexes and displaying, for the first time, a power conversion efficiency > 1 %. What is the excited state reaction scheme for this complex, and how can ^{3}MLCT and ^{3}MC state be distinguished spectroscopically?

Since both states display similar excited state absorption [5], we used femtosecond fluorescence spectroscopy to evaluate the radiative rate of the long-lived excited state and found for $[Fe(bmipc)_2]^{2+}$ in acetonitrile a radiative rate 500-1000 times smaller than the one of the ^{1}MLCT fluorescence [6], in agreement with a dominant ^{3}MLCT character, as opposed to ^{3}MC whose transition is spin and symmetry forbidden. In addition, femtosecond impulsive vibrational spectroscopy (pump-IVS) was performed with 15 fs pulses to obtain the excited state Raman spectrum. Two major features observed are: (I) A strong low frequency Raman activity (~110cm^{-1}) decays completely within the first picosecond after initial excitation. (II) A ≈150 cm^{-1} mode can be reinduced by the push pulse during the 18 ps exc. state lifetime. Normal mode and Raman activity calculations show that these modes are related to global Fe- L breathing modes, in the ^{3}MC and ^{3}MLCT electronic state, respectively [7]. Feature (I) thus clearly demonstrates that excited state ^{3}MLCT/^{3}MC branching occurs also in $[Fe(bmipc)_2]^{2+}$. A detailed analysis of fs TAS and fs-IVS is ongoing in order to determine the branching ratio.

In summary, the present combined experimental and computational study highlights the importance of ultrafast excited state branching in the MLCT/MC manifold for these 4-carbene coordinated Fe(II) complexes with moderate LFSE. The design of novel Fe-based sensitizers needs to take into account, in addition to the LSFE, the dynamic aspects and as much as possible, the excited state energetics along the most prominent reaction coordinates, such as Fe-L bond length changes.

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Communication Orale 04

New lights on Dihydropyrene systems photoisomerization process with theoretical study.

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Figure 1. Photoisomerization of the DHP/CPD photochromic couple (left), push-pull DHP (right).

Dihydropyrene (DHP) is a negative photochromic system which turns into its open-ring cyclophanediene (CPD) form upon light absorption (Figure 1 left).[1] A mechanism for the photoisomerization of DHP was first proposed using a CASPT2//CASSCF computational strategy, relying on CASPT2 energy calculations performed at CASSCF optimized geometries.[2] This strategy suffers from the poor description of the effects of dynamic electron correlation on the optimized structures and on the photochemical reaction path. It is also limited by the system size and the underlying active space required to describe the photoisomerization process.

An alternative way is to use the computationally efficient Spin-Flip Time Dependent Density Functional Theory (SF-TDDFT) method which describes the electronic states of interest and their coupling.[3] A comparative study of the photoisomerization mechanism between CASPT2//CASSCF and SF-TDDFT will be discussed, highlighting some of the differences found. The results obtained by SF-TDDFT calculations are consistent with CASPT2 calculations performed along the SF-TDDFT photochemical reaction path. The application of this method on an extended substituted DHP (Figure 1 right) leads to a new understanding on the more efficient photoconversion of this push-pull system over the bare dihydropyrene.[4]

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Communication Orale 05

Quantum description of the photo-induced electron transfer in gold-organic nanomaterials

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The electron flow between a metallic aggregate and an organic molecule after excitation with light is a crucial step on which are based the hybrid photovoltaic nanomaterials. So far, designing such device with the help of theoretical approaches have been heavily limited by the computational cost of quantum dynamics models able to track the evolution of the excited states over time. In this contribution we present the first application of Time-Dependent Density Functional Tight-Binding (TD-DFTB) method [1] for an experimental nanometer-sized gold-organic system consisting in a hexylprotected Au_{25} cluster labelled with a pyrene fluorophore, in which the fluorescence quenching of the pyrene is attributed to an electron transfer from the metallic cluster to the dye. The full quantum rationalization of the electron transfer is attained through quantum dynamics simulations, highlighting the crucial role of the protecting ligands shell in the electron transfer, as well as the coupling with nuclear movement.[2] This work paves the way towards a fast and accurate theoretical design of optoelectronic nanodevices.

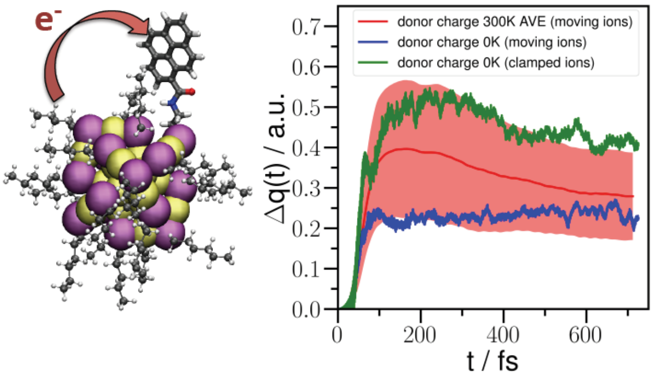

Figure 1. *Functionalized nanocluster under study and computed photoinduced electron flow.*

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Communication Orale 06

Influence of temperature on fluorescence and photo-switching quantum yields for photo-switchable fluorescent proteins: the case of rsEGFP2

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Reversibly photo-switchable fluorescent proteins (rsFPs) can switch between a fluorescent (On) and a non-fluorescent (Off) state (Figure 1). The rsEGFP2 is the reference probe used in RESOLFT super-resolved microscopy. The fluorescence and photo-switching quantum yields of the probe are photo-physical parameters that affect the acquisitions time and the image resolution[1]. These parameters are generally characterized at room temperature. On the contrary, in vivo-imaging is done at 37.5 °C. Here we study the influence of temperature on these parameters. The FP On states are composed by several ground state species originated from the complex hydrogen bond network between the chromophore and the protein cage[2]. This species have different fluorescence lifetimes and therefore can be differentiated with time-resolved fluorescence measurements. Here we report the fluorescence lifetime (τ_{fl}) dependence with temperature to understand the ground state equilibrium of rsEGFP2, and correlate it with the fluorescence quantum yield. Interestingly, our measurements show that the fluorescence is coming from mainly two different conformers with different lifetimes. The longer lifetime is about 2.8 ns and responsible for around 90% of the total emission but represent only 40% of the decay amplitude. The shorter lifetime, which represent 50% of the decay amplitude, lasts 0.15 ns and can be considered as "non-emissive". Strikingly, our temperature dependence absorption spectra show no difference, revealing that the equilibrium between the two conformers is in the sub-millisecond range. Both lifetime constants decrease with increasing temperature, and the shorter lifetime had a three times higher temperature-dependence than the longer one. We could correlate the change in fluorescence with the On-to-Off switching yield. Overall, this work provides insights on the ground-state equilibrium between the two On conformers of rsEGFP2.

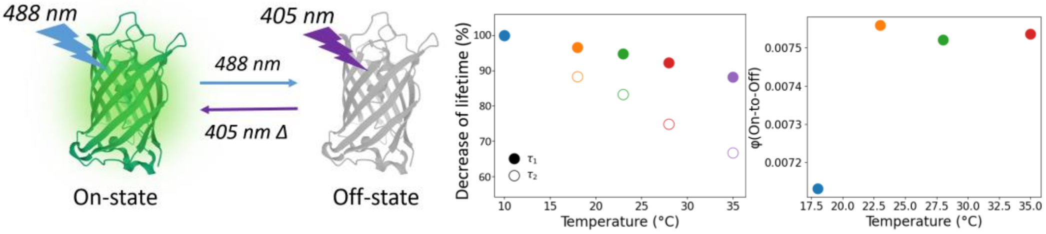

Figure 1. rsEGFP2 photo-switching and temperature-dependence of τ_{fl} and ϕ(On-to-Off)

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Communication Orale 07

Quantification and applications of the NIR-photothermal properties of nickel-bis(dithiolene) complexes

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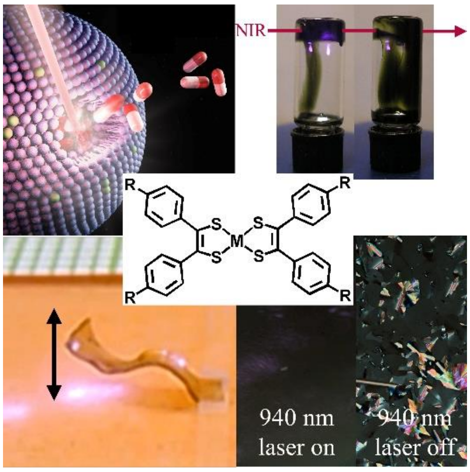
Metal-bis(dithiolene) complexes are known as strong NIR absorbers in a wide range of NIR wavelengths and have been widely used in laser technologies. However, we have recently demonstrated that nickel-bis(dithiolene) complexes also display strong photothermal activities under laser irradiation in the near infrared region which is a of great interest in material science and in biotechnologies.

First, it has been demonstrated that the photothermal activity of liquid crystals built around metal-bis(dithiolene) complexes can be used to stimulate their self-assembly properties under NIR irradiation, making them good candidates for data storage.[1] Water-soluble metal-bis(dithiolene) complexes can also be used to induce cell death under NIR-laser irradiation, highlighting that such complexes can be good candidates for photothermal therapies (PTT).[2] Recent investigations have also demonstrated that NIR irradiation of nickel-bis(dithiolene) containing organic nanoparticles allows the fine control of the release of their drug contents in solution.[3,4] The photothermal properties of metal-bis(dithiolene) complexes have also been used to develop photoresponsive composite material with liquid crystal elastomer (LCE) of high interest in soft robotics.[5] Finally, the photothermal properties of metal-bis(dithiolene) complexes have been properly quantified and a new photothermal index (IPT) allowing to rank molecular photothermal agent have been introduced.[6]



Overview of the systems presented

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Communication Orale 08

Ligand-Driven Light switching of Single Molecule Magnets

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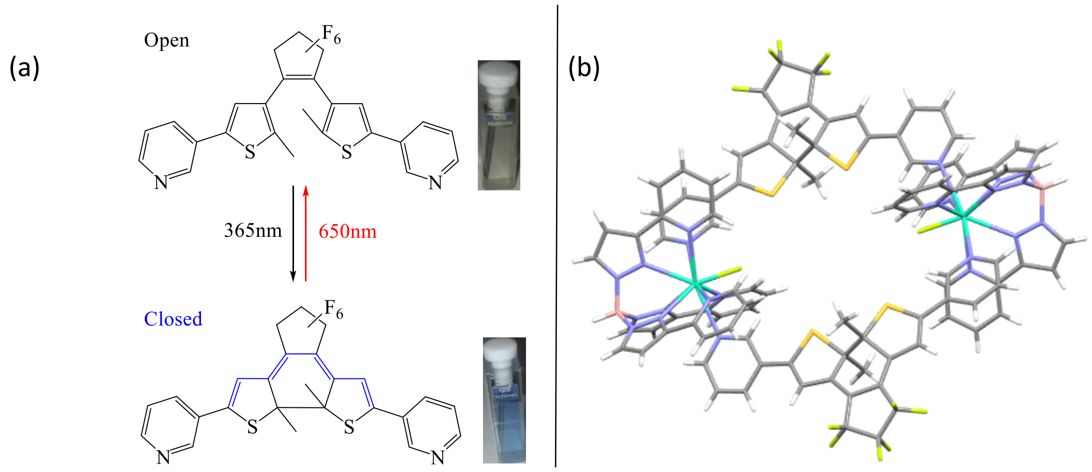
Single Molecule Magnets (SMM) are molecules that behave as tiny magnets at low temperature. SMM offers unique features that may allow information to be stored with much higher densities, and to be processed at unprecedented speeds. [1] In order to use SMM in information storage devices, it would be a great advantage to control the magnetic properties by applying an external stimuli. Light is fascinating in this purpose due to its easy and contactless application. [2]

The goal of our project is to create an efficient strategy to switch reversibly the molecular magnetic behavior with light, relying on the photochromic abilities of a ligand, and on the recognized influence of the coordination environment on the SMM property.



(a) Photochromic transformation of a DTE molecule **(b)** Cationic cage assembled with DTE and Dy-F units

In our target complexes, we aim to control the slow relaxation behavior of dysprosium (III) complexes through the photoisomerization of a dithienylethene (DTE) molecule that is known to show good photo-reversibility and excellent thermal stability for both opened and closed forms. [3] In this presentation, I will introduce a strategy to photo-switch reversibly the SMM behavior based on a supramolecular approach. [4]

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Communication Orale 09

Modulation of arene-Ru^{II} complexes structures and properties with *ortho*-sulfonamide azobenzene ligands

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The external manipulation of molecular systems with light is being increasingly exploited for the control of events at various scale, eventually giving rise to "smart" systems, with applications in the field of biology, material science or catalysis. [1]

Arene-Ru^{II} complexes bearing *ortho*-sulfonamide azobenzene ligands display a great diversity of structures, with coordination patterns such as **exo-*E***, **exo-*Z*** and **endo-*E*** (Figure 1). [2] Here, we will report the results of a systematic study aiming to understand the influence of substituents (R, R' and X) on the structure and photophysical properties of this type of complexes.

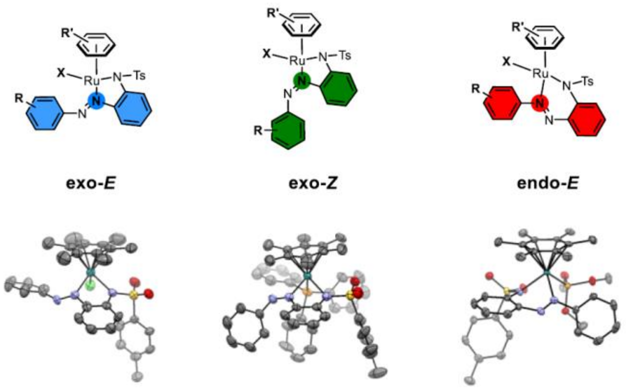

Figure 1. Coordination patterns of arene-Ru^{II} complexes bearing *o*-sulfonamide azobenzene ligands

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Communication Orale 10

Modelling absorption and emission spectra taking into account the dynamic environment: example of firefly bioluminescent systems and analogues

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The emitting light in fireflies or other bioluminescent species arises from the electronic relaxation of oxyluciferin, an organic compound resulting from the oxidation of the D-luciferin substrate inside an enzyme called luciferase. In order to have insight of the mechanism of the light emission, both experimental and theoretical joint studies have been performed. Absorption and fluorescence spectra of the products of the bioluminescence are obtained by a combination of molecular dynamics (MD) followed by calculation of the electronic transitions by hybrid (QM/MM) methods. The emission and absorption spectra are accurately reproduced compared to the experimental ones when the dynamic of the system is taking into account.

I will present briefly the used methodology and examples of theoretical studies that can give complementary insights to the experimental results.

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Communication Orale 11

Octahedral Molybdenum clusters containing hybrid materials: from their synthesis to their studies on the Caphter platform

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Metal clusters are nanometric assemblies of metal atoms maintained by metal–metal bonds. Within this compound family, octahedral cluster compounds of general formula $A_nM_6X^i_8L^a_6$ (A=alkali cation; M: Mo, W, Re; X^i: halogen, chalcogen; L^a: anion) are obtained by solid-state chemistry routes and show a stable phosphorescence in the red-NIR with high quantum yield values. Here, we will show how, by taking advantage of $A_2M_6X^i_8L^a_6$ cluster specificities, we integrate them homogeneously in soft organic matrices like liquid crystal[1] or polymer[2]. The photophysical studies realized on the Caphter Platform (UER ScanMAT, Rennes), demonstrate that obtained hybrids combine the host matrix properties and the metal clusters red-NIR emission. They have potential in applications like oxygen sensors, theranostic, photocatalysis, optoelectronic, lighting or smart windows. Adding complementary emitters within such hybrids enhances their emission abilities and response toward external stimuli.[3]

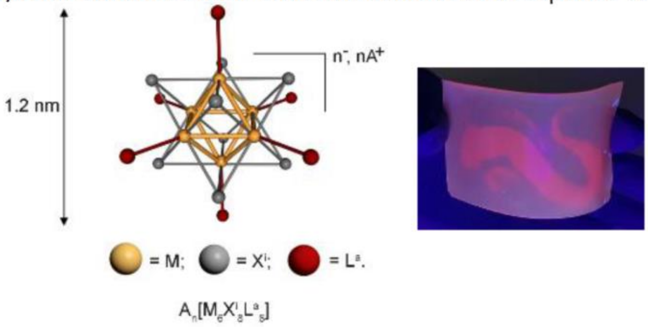

Figure 1. left: Schematic representation of a cluster compound; right: PMMA sheet doped with a cluster compound and a complementary luminophore under UV-A.

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Communication Orale 12

Fluorescence switching with bisphosphonium

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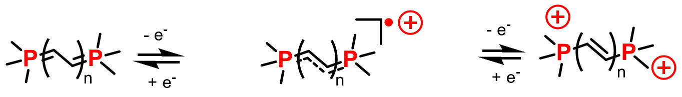
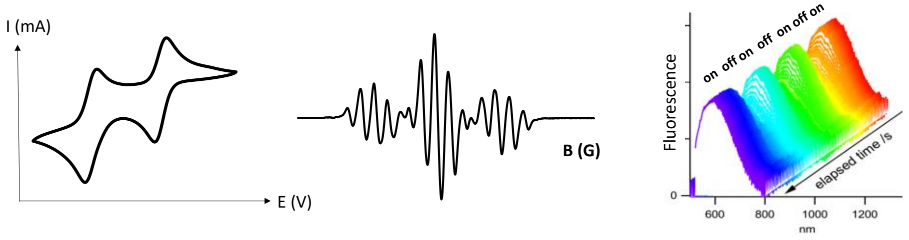
Organic multi-stage redox systems are key component in many technological fields ranging from organic electronic (solar cells, batteries…) to spintronic. Among the strategies used to design such compounds, one approach consists in linking two cationic heteroatoms through a π-conjugated backbone featuring an even number of *sp*^{2} C-atoms.[1] This led to the preparation of "Weitz type" derivatives with three stable redox states including a stable radical cation intermediate. Methyl-Viologens (MV) are probably the most emblematic electron acceptors of this family.[2] Although Hünig *et al.* mentioned the applicability of this general strategy to systems in which phosphorus is the unique heteroatom (see Fig.), such derivatives were been described yet to the best of our knowledge, despite the wide literature on organophosphorus based π-systems and switches. To tackle this challenge, we here take advantage of the possibility to convert a cationic $\sigma^4\lambda^4$ P^+-atom into a neutral $\sigma^4\lambda^5$ P (Fig.) to afford multi-stage redox systems based on organophosphorus derivatives. Indeed we report the straightforward synthesis of an unprecedented family of dicationic P-containing Polycyclic Aromatic Hydrocarbons (PAHs) where two $\sigma^4\lambda^4$ P^+ atoms are connected through various PAH backbones. The effect of π-extension on both the optical and redox properties is investigated using a joint experimental/theoretical approach. Spectroelectrochemical studies prove that these compounds possess three stable redox states and EPR studies confirms the *in situ* formation of radicals demonstrating that these novel acceptors possess a "viologens-like" redox behaviour. Finally, electrochemical modulation of fluorescence performed on two compounds highlights the potential of these intrinsically switchable electroactive fluorophores.[3]



Intrinsically switchable electroactive fluorophores



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Communication Orale 13

Synthesis and characterization of atropoisomeric pyrene- based dithienylethenes: Optical control of luminescence properties

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Luminescent molecules are present in a wide variety of domains, such as biology (bio-imaging), optoelectronics (data processing, molecular storage) and electroluminescent devices that are now part of our daily lives (OLED screens). In this highly competitive field, our approach aims to bring two additional dimensions:

i)The control of the luminescence by light

ii)The introduction of chirality by atropoisomerism

Based on our expertise in the synthesis and study of photochromic dithienylethenes (DTE), [1] we designed new pyrene-based DTEs that should gather luminescence and chirality, in order to access light-switchable circularly polarized luminescence. [2]

Our strategy toward atropoisomeric DTEs relates on blocking the interconversion between the two antiparallel conformations, by judicious structural modifications of the DTE core (see figure). The obtained racemic mixture of atropoisomeric DTEs will thus be separable upon chiral HPLC. The two pyrenes are positioned in a face to face fashion to produce an excimeric emission, only in the DTE's open form. The photochromic reaction of the DTE will reversibly switch the excimeric luminescence, in a chiral environment. [3] DFT calculations are conducted to study the dynamics of our systems.

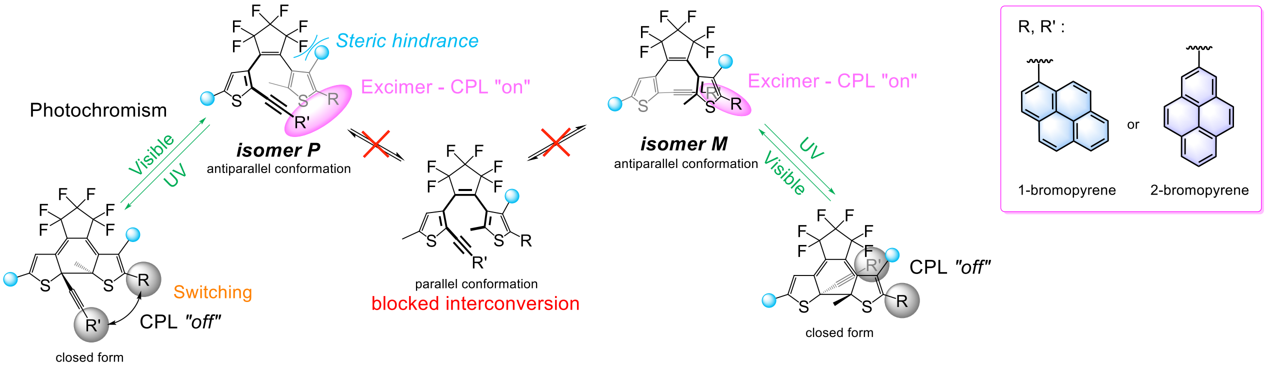

Figure 1. Design of the atropoisomeric pyrene- based DTEs and blocking of the interconversion by atropoisomerism.

The design strategy and the synthetic pathways, along with the optical properties of the synthetized molecules will be presented. The results of the following of the photochromism by ^{1}H and ^{19}F NMR and UV-Visible absorption will be discussed. The dynamic of the system was also studied via variable temperature experiments.

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Communication Orale 14

Fluorescence photoswitching of diarylethene dyads: from energy transfer to unconventional behavior and photokinetics

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Photochromic/fluorescent dyad leads to photoswitchable emissive systems through energy transfer processes.[1] The profile of the response between the fluorescence signal and the conversion yield of the photochromic moiety depends on the environment. When the dyads are gathered in nanoparticles states, giant amplification effect leading to a nonlinear profile can be observed.[2] Design and synthesis of new diarylethene/perylenediimide architectures will be presented.[2] Steady-state spectroscopy in solution and nanoparticles revealed uncommon properties depending on the ratio of diarylethene in the compound. Time-resolved spectroscopy was carried out to investigate and characterize the energy transfer processes. Moreover, they also impact the photokinetics that can be finely tuned depending on the irradiation wavelength, leading in some cases to an unconventional "pseudo zero order" effect. To explain such an interesting behavior, a mathematical modeling was achieved, allowing the determination of the photochromic quantum yields.

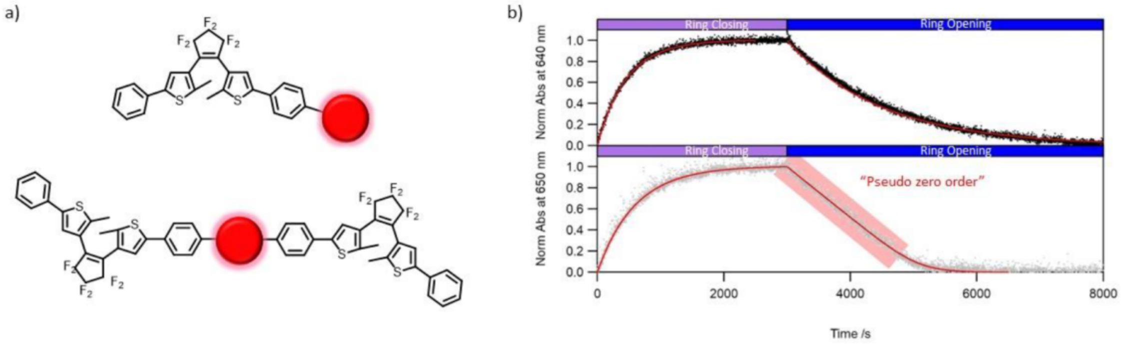

Figure 1. a) Schemes of diarylethene derivatives linked to fluorophores (red circles), b) photokinetics of the dyads in solution (black dots, classical profiles are obtained) and photokinetics of a colloidal suspension of nanoparticles (grey dots, unconventional "pseudo zero order" kinetic profile is revealed under specific irradiation wavelengths).

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Communication Orale 15

1,1,4,4-tetracyanobutadienes derived from ynamides: new fluorophores sensitive to their environment

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Tetracyanoethylene (TCNE) is well known for reacting with some electron-rich alkynes to lead to 1,1,4,4-tetracyanobutadienes (TCBDs) in variable yields.[1] This reaction processes according to a [2+2]cycloaddition-retroelectrocyclization sequence. In particular, we showed that ynamides are good partners to lead to TCBDs in high yields.[2] Although TCBDs have long been considered as non-fluorescent compounds,[3] we have recently shown that some TCBDs derived from ynamides are able to emit light, depending on their environment. In particular, they are very sensitive to the polarity of the solvent they are dissolved in.[4] They are also able to emit light in near-infrared region in the solid state until 1550 nm if they are connected to a pyrene, a perylene or anthracenes (Figure 1).[5]

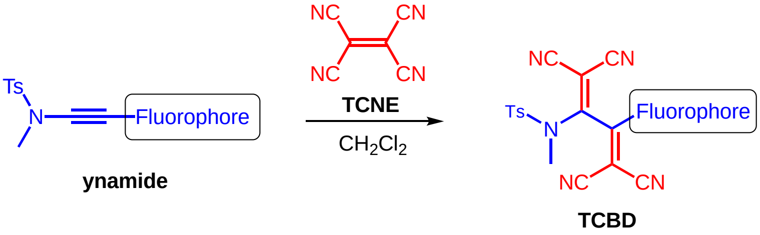

Figure 1. Synthesis of TCBDs connected to fluorophore from their corresponding ynamides.

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Communication Orale 16

Annulée

Preparation and study of luminescent Cu(I) multinuclear assemblies

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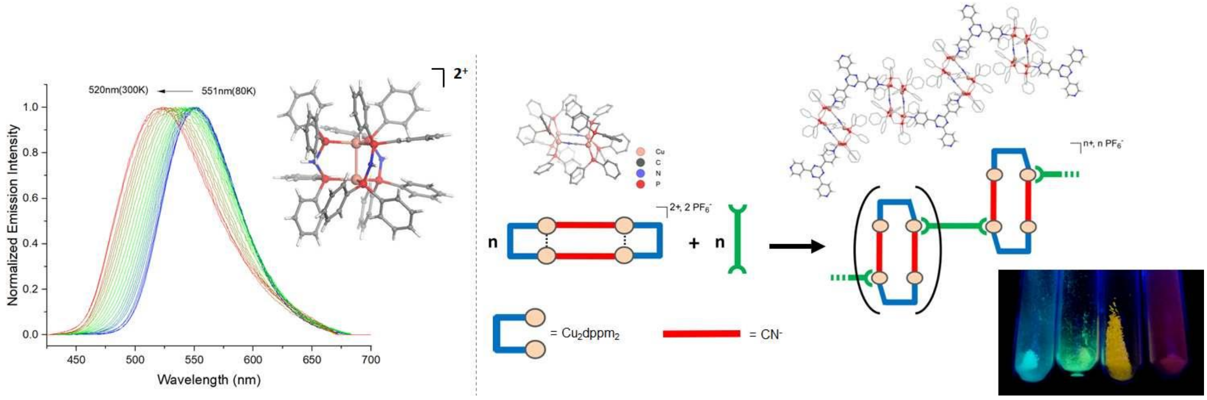
An increasing interest is devoted to Cu(I) metal complexes for the preparation of new multifunctional molecular materials for lighting and sensors applications.[1] We will present the straightforward syntheses and solid-state characterizations of novel series of polymetallic Cu(I) supramolecular assemblies. Taking advantage of the unique conformational flexibility that the Cu(I) ion coordination sphere presents,[1a,2] very diverse multinuclear architectures are obtained, associated with a large variety of photophysical properties. [3]



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Communication Orale 17

Design of macrocycles as versatile visible-light photoinitiators for bulk free-radical and cationic polymerizations

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Macrocyclic molecules such as porphyrins (Pps) and phthalocyanines (Pcs) constitute an unlimited library of structures with versatile and fascinating chemistry. Certain features, such as unique electrochemical, photochemical and photophysical properties have opened a multitude of applications, ranging from photodynamic therapy in cancer treatment, chemical sensors, solar cells, nonlinear optics, and recently to photoinitiating systems for controlled radical, free-radical and cationic polymerizations.[1,2] Thanks to their exceptional absorption spectra, some macrocycle-based systems could initiate polymerization up to red-light and NIR irradiation.

Many studies reported the use of macrocycles as highly performing photoinitiators (PIs) for bulk polymerization. Widely studied as photosensitizers for iodonium salts,[3] it appeared recently that they could also induce inter- or intra-molecular H-abstraction in presence of amine groups.[4] Besides, incredible versatility of macrocycles allows them to be more than simple PIs. For instance, they can play a double role of photosensitizers for photo-dynamic therapy, leading to inactivation of bacterial cells on polymer surfaces.[5] Silver-complexed Pcs were also proposed for one-pot photo-induced synthesis of nanocomposites.[6] Despite a growing interest, initiation mechanisms by macrocycles remain poorly understood: Their structural variety seems to lead to an equal variety of mechanisms, offering huge opportunities of investigations.

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Communication Orale 18

Pyrrolopyrrole cyanine dyes as Near InfraRed photosensitizer for hydrogen production via water reduction using Dye Sensitized Photocatalysis system

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The conversion of sunlight into chemical energy is a promising solution to accompany the energy transition and limit global warming. Hydrogen is a particularly attractive energy vector because it could meet 18% of the world's energy demand by 2050.[1] Among the various approaches to convert solar energy into hydrogen, DSPs (Dye Sensitized Photocatalytic) are particularly suitable because they are easy to manufacture and they are based on low cost materials.[2] Such devices rely on electron transfer between a photosensitizer co-grafted with a proton reduction catalyst on nanoparticles of a semiconductor such as TiO_2 (Figure 1). However, most of the sensitizers integrated in these systems absorb only in the visible range and very little in the NIR. There is only a handful examples of reports with phthalocyanines[3] and squaraines towards this objective but with limited efficiencies.[4] In study, we have extended the field of application of pyrrolopyrrole cyanine dyes (PPcys) to DSPs systems for hydrogen production. Indeed, PPcys have proved to be currently the most efficient NIR dyes for transparent and colorless DSSC (Dye Sensitized Solar Cell).[5] This presentation focuses on hydrogen production with DSP sensitized with PPcy. We demonstrate the potential of this class of dyes to evolve hydrogen with low energy photon (> 750 nm) with unmet performances.

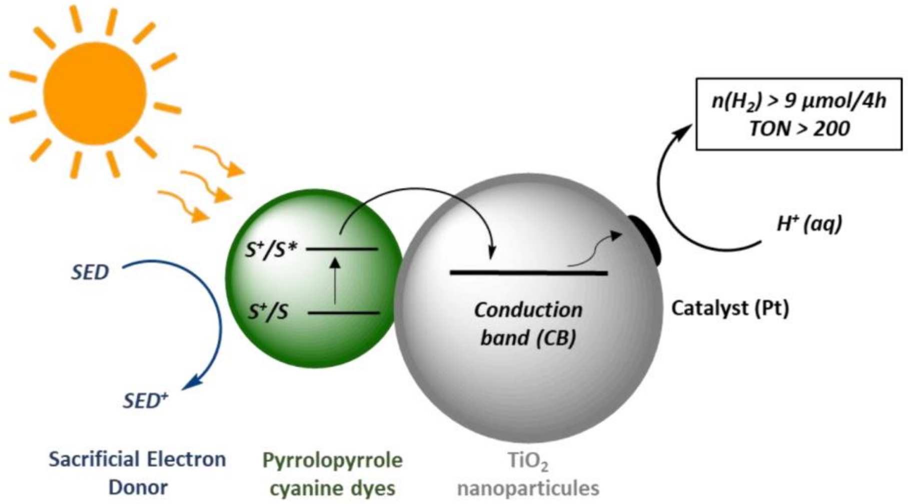

Figure 1. Illustration of the working principle of a DSP system.

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Communication Orale 19

Photo-isomérisation sélective de l'acide salicylique

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L'acide salicylique, un précurseur dans la synthèse de l'aspirine, est une molécule qui présente plusieurs isomères : la forme E (la plus stable), la forme R et la forme H ont été observées [1]. Notre objectif est de caractériser et comprendre la formation par irradiation UV de ses différents isomères, en les piégeant dans un solide d'argon. On a ainsi observé des émissions de phosphorescence et de fluorescence grâce à un laser accordable. En mettant en évidence les corrélations entre ces émissions et les spectres d'absorption infrarouge et UV, on a pu attribuer une fluorescence entre 360 et 450nm à la forme E (τ<9ns) et des émissions de phosphorescences aux formes R et H (τ>1,5s) (cf. Figure 1). Nous avons également montré qu'il était possible de convertir un isomère en un autre en irradiant l'échantillon à des longueurs d'ondes spécifiques.

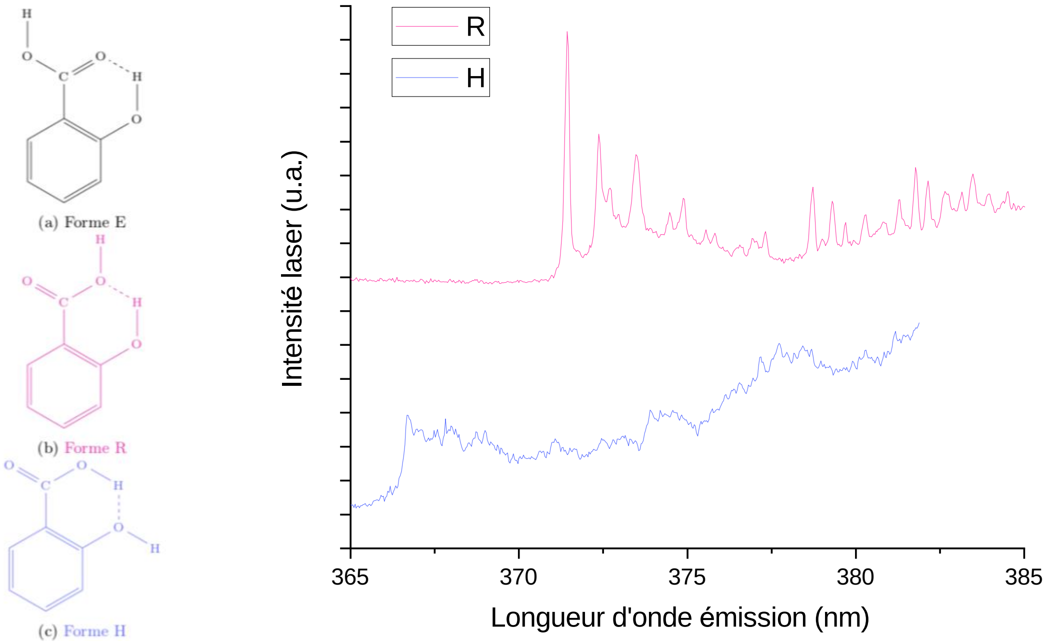

Figure 1. À gauche, les différents isomères de l'acide salicylique observés. Au centre, l'émission de phosphorescence de la forme R (excitation à 315,5nm). À droite, l'émission de phosphorescence de la forme H (excitation à 295,3nm).

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RESUMES

Posters

Poster 01

Optical spectroscopic investigation of a sol-gel process for dyeing textiles

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Textile dyeing began thousands of years ago, when plants and insects were used as sources of natural dyes for drawing and dyeing. With the development of man-made synthetic dyes, the textile dyeing industry evolved quickly and developed many successful dyeing processes. However, these processes consume large amounts of energy, chemicals and generate harmful waste water. We are currently exploring a low-temperature sol-gel process (Figure) for dyeing textiles with the aim to reduce energy and chemicals consumption. The sol-gel process is expected to form a three-dimensional silicate network encapsulating the dye and adhering to the textile fibers.[1] The sol-gel precursors can be chemically modified to incorporate further functionalities (*e.g.,* energy harvesting, luminescence).

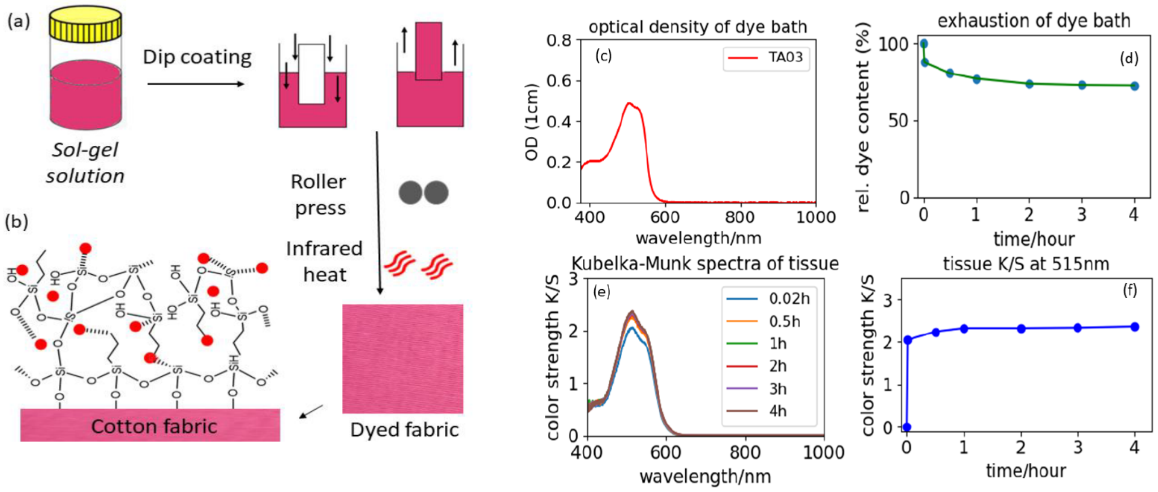

Figure. a) Sol-gel-dyeing process for cotton fabric. b) Proposed structure of the deposited dyed sol-gel layer. (c + d) absorbance spectrum of the dye in solution and dye bath monitoring. (e+f) The Kubelka-Munk spectrum of dyed textile and monitoring of textile dye content.

In our study, we monitored the evolution of the dyeing bath containing the dye and the sol-gel reactants (*e.g.*, decrease in dye content during the process) using absorbance spectroscopy (Beer-Lambert-Bouguer). We also measured the final dyed fabric using diffuse reflectance spectroscopy (Kubelka-Munk). Using these measurements, we optimized the dye process parameters and propose an optimized sol-gel dyeing process working at low temperatures (30°C) and using fewer solvents. The sol-gel process can now be modified to incorporate other materials, such as luminescent particles.

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Poster 02

Photon- and electron-induced modification of coordination pattern in arene ruthenium complexes

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Arene ruthenium complexes of type **1**–**5**, containing azobispyridine or tosylamide azobenzene ligands, were shown to exhibit various coordination patterns depending on the steric and electronic nature of **R**, **X** and **L** groups (Fig. 1).[1,2,3]

In response to light or electrochemical stimuli, many of them undergo isomerization at the N=N bond of azobenzene core associated with a modification of coordination pattern or de-coordination of ligand **L** from the metal center.

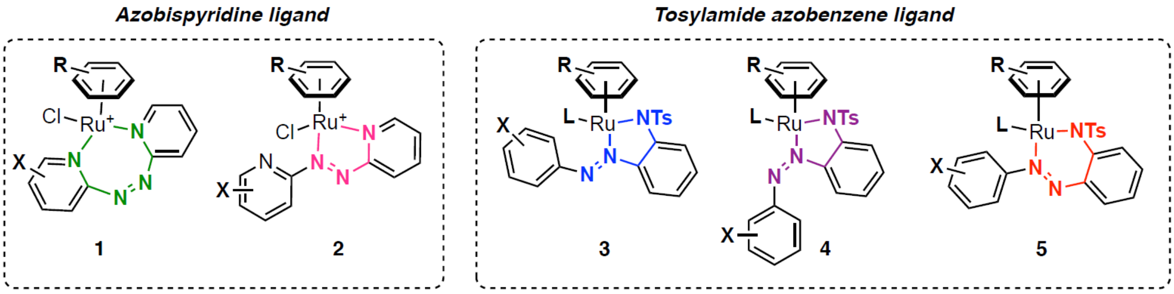

Figure 1. General structure of two families of azobenzene-derived ruthenium complexes.

An overview of the synthesis and properties of such families of complexes will be presented, emphasizing latest results related to stimulation with photons and/or electrons, and perspectives towards initiation of catalytic activity.

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Poster 03

Experimental studies of non-linear optical properties of photo-stimulable switches based on Stenhouse adducts

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We have studied the linear and non-linear optical (NLO) properties of a set of Stenhouse adduct derivatives. These compounds have the peculiarity of switching under irradiation between a colored and hydrophobic conjugated form, into a colorless and hydrophilic closed ring[1,2,3]. The contrast in molecular hyperpolarizability between the two forms is due to a large change in the electronic distribution between these two forms. Photoswitching kinetics of the absorption spectra were recorded in situ in real time for an irradiation centered at 560 nm and covering the entire absorption band of the colored form (see Figure 1). Hyper-Rayleigh scattering (HRS) measurements under in-situ irradiation were performed for the first time.

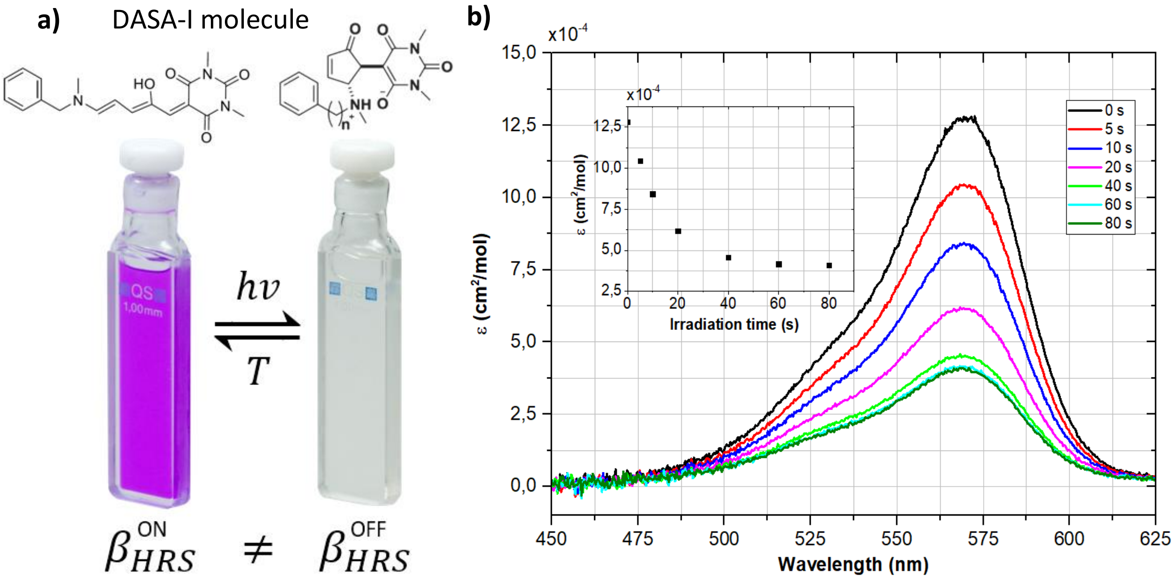

Figure 1. a) DASA-I in its linear state (left), and in its cyclic state (right). b) Photoswitching kinetics of DASA-I under 16 mW/cm^2 irradiation.

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Poster 04

Grafted difluoroboron β-diketonates derivatives, towards mechanofluorochromic surfaces

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Boron difluoride β-diketonates (DFBs) have been shown to exhibit mechanofluorochromism (MFC), a phenomenon where mechanical stimulation induces a typically reversible change in their fluorescence properties, as powder or deposited materials.[1] A DFB derivative bearing a triethoxysilane functional group was synthesized to allow the functionalization of glass substrates (Fig. 1). The photophysical and MFC properties of DFB grafted on glass were characterized and compared to solution, powder, and drop-casted forms, via steady-state and time-resolved spectroscopy. Thermal annealing of the drop-casted samples caused a hypsochromic shift in the maximum fluorescence emission wavelength indicating a return to a more arranged structure. This was not observed in the grafted systems, where MFC was lost after thermal annealing. Studying functional surfaces can potentially extend MFC applications to new fields, such as microfluidics.

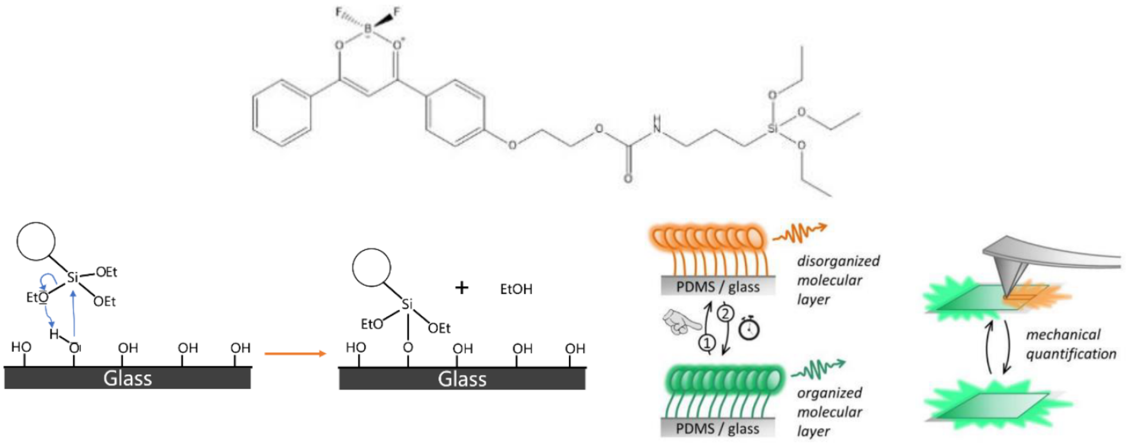

Figure 1. The synthesized DFB Derivative (**top**) together with the grafting mechanism (**bottom left**) and the principle of MFC on surfaces (**bottom right**).

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Poster 05

Fluorescence Observation of Spatiotemporal Heterogeneity of Aggregation Structure in Thin Film by Difluoroboron β-Diketonate Dyes

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For the development of next-generation flexible OLED devices, the drop-casting method has been attracting attention as a technology for forming thin films easily and at a low cost. Therefore, investigating the aggregation dynamics of the formation of films during the drop-casting process is important for the development of fundamental understanding in this field. In this study, Hyperspectral camera (HSC) fluorescence imaging was newly applied to evaluate spatiotemporal heterogeneity in the thin film, collecting the fluorescence spectra from each region of the sample. Figure 1 shows the spatial-resolved fluorescence spectra of difluoroboron β-diketonate dyes (BF_2DBMb) casting from the solution.[1][2] As future work, we expand the system to CPL to observe molecular conformation and orientation in the thin film. We are now working on synthesizing new types of β-diketonate compounds which exhibit different circularly-polarized luminescence properties (CPL) depending on the aggregation structure [3].

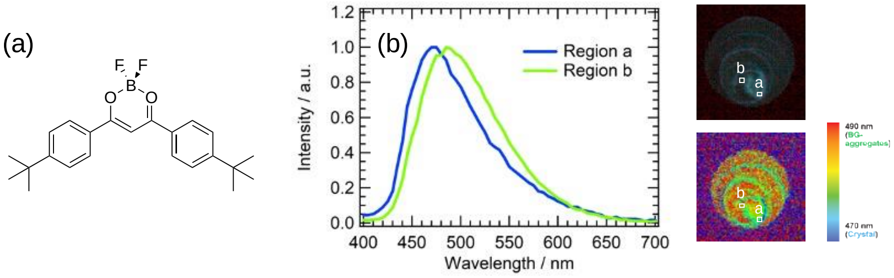

Figure 1. (a) Molecular structure of BF_2DBMb, (b) Fluorescence spectra, fluorescence image and spectral color mapping of a drop-casted film after evaporation obtained by HSC.

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Poster 06

Direct Deep UV (DUV) photopatterning of metal oxide thin films from nanocrystal (NCs) colloids: a simpler and faster process at room temperature

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Deep UV photolithography (193 nm) is a reference technique for micro/nanopatterning. The photoresists used, which are exclusively organic, have only a sacrificial role and do not contribute to the final properties of the material. This also adds a significant number of steps and the use of corrosive products in the process. In the case of metal oxides, several studies have already made it possible to considerably reduce the number of steps by directly structuring the material using hybrid photoresists [1, 2]. The produced oxide is however amorphous and a high-temperature annealing step is necessary to obtain the crystalline phase, ruling out the application to flexible substrates. A possible solution is to start directly from the oxide in the form of NCs and to assemble them. This approach has already been successfully tested in the case of quantum dots (CdS, CdSe) and for micrometric resolutions [3] but always involving toxic products. The objective is to propose an original direct nanopatterning approach using colloidal NCs as "building blocks" that assemble under the effect of DUV light, while being more environmentally friendly (abundance, toxicity).

Using FTIR and XPS spectrocopies, ellispsometry and XRD characterizations, it has been observed that the assembly of NCs results from a spatially controlled aggregation following the degradation of ligands on the surface without modification in size of the NCs (**Fig. 1**). The study focuses mainly on ZnO but the wide variety of oxides that can be synthesised in the form of NCs encourages a generalisation of the process to other oxides.

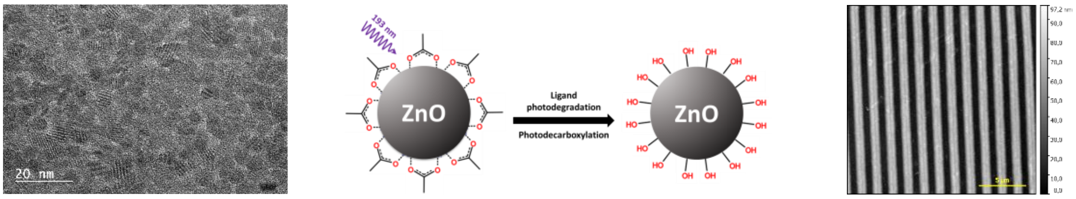

Figure 1. From colloids to microstructures by ligand photodegradation under DUV exposure.

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Poster 07

Diphenyl functional porphyrins and their metalcomplexes as visible-light photoinitiators for free-radical, cationic and thiol–ene polymerizations

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Photoactive polymers have shown increasing interest in recent years. Indeed, these materials contain photoactive molecules able of producing cytotoxic species under visible light such as reactive oxygen species (ROS). This could allow to kill bacteria in contact with the surface autonomously.

These polymers would be synthesized by photopolymerization, which is generally considered as a more economical and safer chemistry. Indeed, photochemical reactions occur in minutes, at low energy cost, under mild conditions and with few organic solvents. Many types of photoinitiators have already been developed to enable radical or cationic photopolymerization [1], but recently there has been a growing interest in new structures that absorb long wavelengths in the visible-light or near infrared range, such as porphyrin derivatives [2], [3]. Using visible light allows the use of harmless and economic lamps, such as LEDs.

New molecules derived from porphyrin would be synthesized to initiate photopolymerization in the visible range. After polymerization, these photoinitiators would remain trapped in the matrix. Upon irradiation, they could react with oxygen to produce ROS causing bacteria's death.

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Poster 08

SYNTHESIS AND PROPERTIES OF AZOBENZENE-DERIVED POROUS COORDINATION POLYMERS

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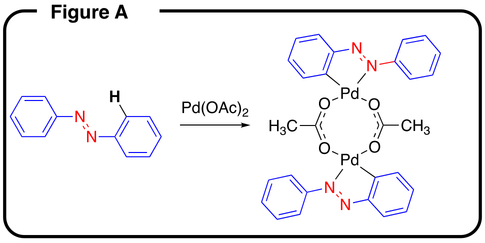
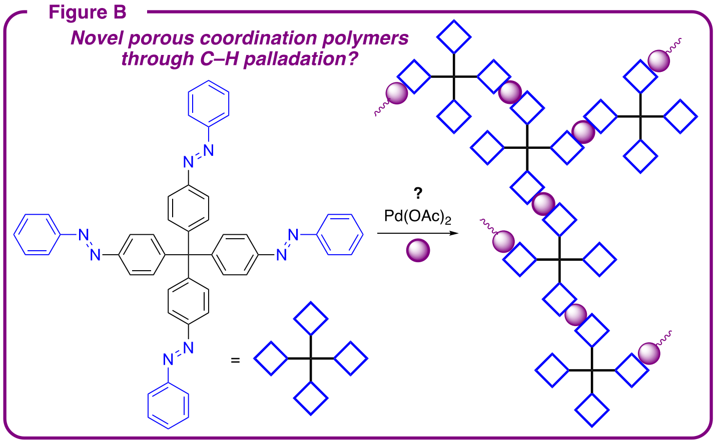
Porous materials have gained a strong interest over the last decades for their potential applications in a variety of fields such as drug delivery, gas adsorption and separation, energy storage, photocatalysis and photoluminescence.[1]

In the continuation of our previous work dealing with azobenzene-derived porous organic polymers,[2] we wish to take advantage of the ease of C–H palladation reaction of azobenzene derivatives (Figure A) to create novel porous coordination polymers (Figure B).



Azobenzene dimerization through C–H palladation



Novel porous coordination polymers through C–H palladation?

The synthesis and properties of some azobenzene-Pd coordination polymers will be presented, as well as perspectives for their utilization as photon- and electron-responsive materials.

References:

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Poster 09

Giant amplification effect of fluorescence photoswitching in organic nanoparticles investigated by spectroscopy and microscopy

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Fluorescence modulation of emissive system can be achieved by attaching a photochromic unit to a fluorophore. In this context, we studied covalently-linked diarylethene/perylenediimide architectures, with different ratio of each building block.[1] Molecular dyads in solution present a linear correlation profile between the fluorescence signal and the conversion yield of the photochromic molecule whereas a giant amplification effect appears when the dyads are gathered in organic nanoparticles.[2] This energy transfer in solution and in nanoparticles was characterized by fluorescence anisotropy and fluorescence decay. Microscopy studies at the level of single nano-objects will be presented, allowing us to follow, in real time, the fluorescence modulation of the nanoparticles (cf. Figure 1).

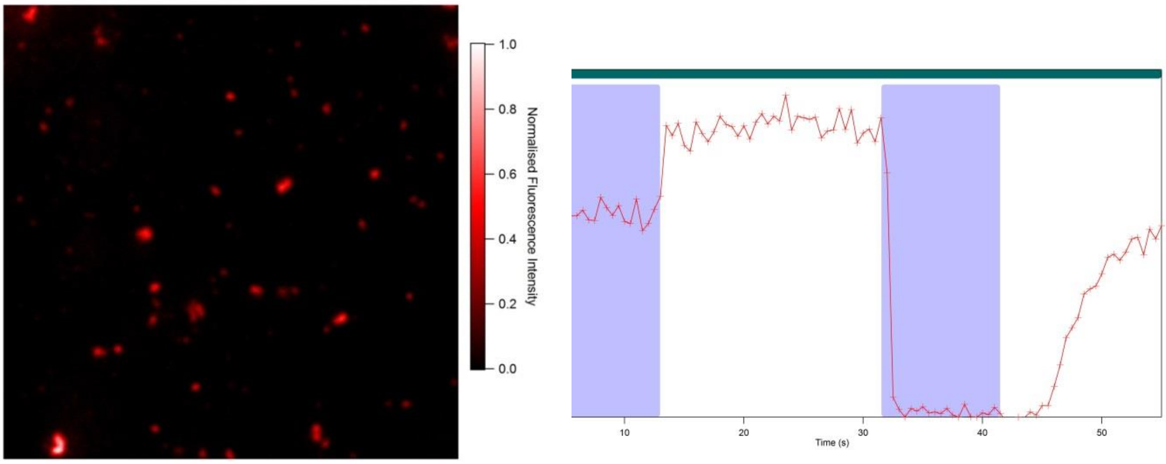

Figure 1. Fluorescence microsocopy image and intensity timetrace showing fluorescence photoswitching (under UV light) with different irradiation powers.

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[2] T. Fukaminato, S. Ishida, R. Métivier, *NPG Asia Mater.* **2018**, 10, 859-881

Poster 10

FROM NANOSCOPIC MOLECULAR PHOTODECAGING TO MICROCAPSULE EXPLOSION : UPSCALING PHOTORELEASE

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Molecular-scale photodecaging has been shown to lead to programmable rupture of cell-sized vesicles, with particular emphasis on self-assembled polymersome capsules.[1] As a result, photoliberation of molecular cargo in pseudo-physiological conditions is demonstrated. Snapshots of a real-time micrometric polymersome explosion under irradiation is shown in the Figure 1.

The mechanism involves a hypotonic osmotic imbalance created by the accumulation of photogenerated species inside the lumen, as a result of photodecaging. As this cannot be compensated owing to the low water permeability of the membrane vesicle, a rupture occurs and contents are liberated. This simple and versatile mechanism can be adapted to a wealth of hydrosoluble dye molecules, which are either able to generate reactive oxygen species or undergo photocleavage, offering high spectral and spatio-temporal control. Current works seeks to develop biocompatible systems involving different copolymers and several water-soluble dyes, affording photoactivity across the visible spectrum.

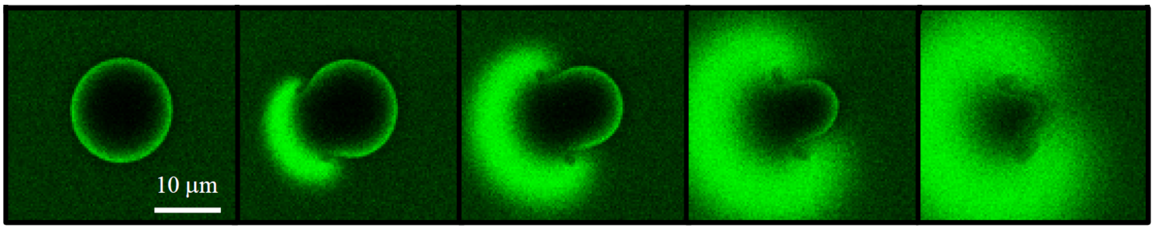

Figure 1 : Snapshots of a photodriven polymersome explosion under irradiation at 488 nm (confocal fluorescence microscope observation, each frame is separated by 70 ms).

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Poster 11

Etude des états triplet de Tetraphenyl porphyrine de cuivre et d'Octaelthyl porphyrine du cuivre

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Les états triplets ne peuvent pas être excités directement par un ou plusieurs photons à partir d'un état fondamental singulet à cause des règles de sélection. C'est pourquoi ces états ont des durées de vie longues et peuvent être considérés comme des réservoirs d'énergie ou des intermédiaires réactionnels efficaces. C'est le cas des photosensibilisateurs utilisés pour la photothérapie dynamique : Il s'agit d'administrer des molécules photoactivables très souvent des dérivés porphyriniques, qui, une fois photoexcités se trouvent dans un état triplet à longue durée de vie leur permettant de transférer leur énergie à du dioxygène environnant. Après collision avec l'état triplet le dioxygène passe dans un état singulet ($^1\Sigma_g^+$, $^1\Delta_g$) métastable très réactif qui détruits tous les cellules vivantes environnant et en particulier les cellules tumorales. .

Dans ce travail on a mis en évidence l'existence des états triplet de Tétraphenyl Porphyrine du Cuivre (CuTPP) et d'Octaethyl Porphyrine du Cuivre (CuOEP). En utilisant l'ionisation multi photonique femtoseconde et on a déterminé leur durée de vie en utilisant l'ionisation nanoseconde. Ces états triplet de longue durée de vie ont permis de mettre en place une méthode pour observer le spectre d'action de l'état S1 de CuTPP et de CuOEP qui ont une durée de vie ultracourte en utilisant les lasers nanosecond.

L'étape suivante de ce travail est d'étudier les collisions entre un état triplet de porphyrine et le dioxygène pour déterminer le mécanisme de transfert d'énergie de la porphyrine vers le dioxygène. Ce travail se fera dans un piège à ion refroidi où aura lieu des collisions entre des anions porphyriniques et le dioxygène. Les anions porphyrines seront habillées avec des (SO_3^-) en périphérie de leur nuage électronique π, ce qui modifie peu leur relaxation électronique[1].

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