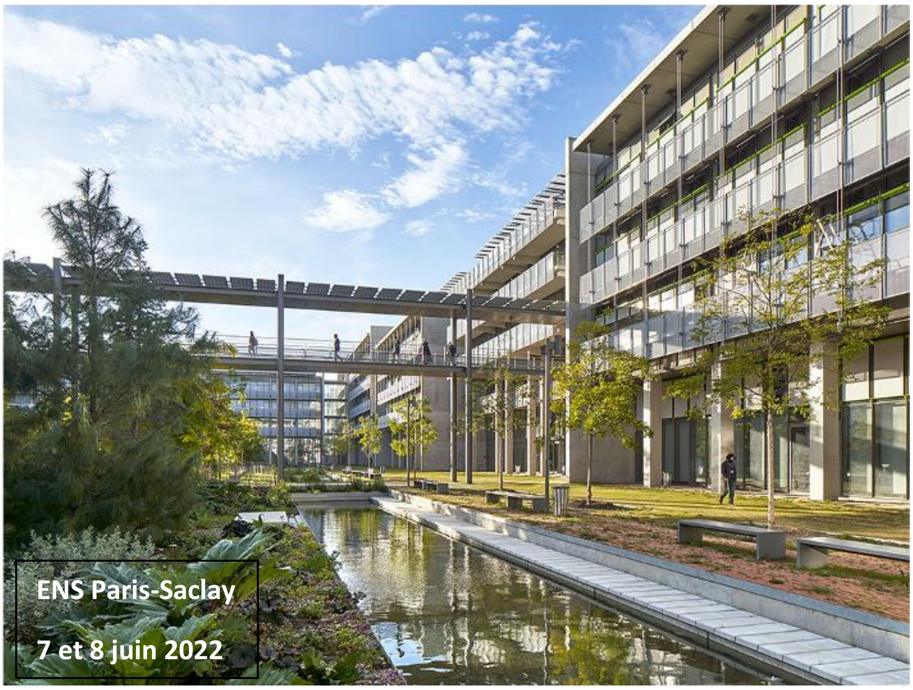
Journées Annuelles SP2P

Edition 2022

Subdivision Photochimie, Photophysique, Photosciences

Division Chimie-Physique (DCP)

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



ENS Paris-Saclay

7 et 8 juin 2022

MOTS D'ACCUEIL

Nous sommes ravis de vous accueillir ces 7 et 8 juin 2022 à l'ENS Paris-Saclay pour deux journées de conférences autour de la photochimie, de la photophysique et de spectroscopies variées.

Les Journées Annuelles 2022 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, représentent une excellente occasion de réunir la communauté des photochimistes et photophysiciens, avec la possibilité pour les étudiants et jeunes chercheurs de présenter leurs travaux, dans une atmosphère détendue, constructive et bienveillante.

C'est aussi la chance de pouvoir écouter des chercheurs confirmés, expérimentateurs ou théoriciens renommés. Pour cette édition 2022, nous avons l'honneur d'accueillir plusieurs conférencières et conférenciers invités :

- Michael Oelgemöller (Keynote, Fresenius Univ. Applied Science, Allemagne)
- Aurélie Perrier (Univ. Paris Cité / Univ. PSL)
- Marie-Claire Schanne-Klein (École Polytechnique)
- Guillaume Schull (Univ. Strasbourg)

Une session spéciale en hommage au professeur Jean Faure (1935-2017), emblématique de la photochimie en France, est prévue le mardi 7 juin en fin de journée.

Enfin, une visite des laboratoires du PPSM, récemment implantés à l'ENS Paris-Saclay, est organisée le mercredi 8 juin midi.

Nous vous souhaitons la bienvenue et nous espérons que vous profiterez pleinement de ces Journées !

Le comité d'organisation

Comment venir à l'ENS Paris-Saclay ?

ENS Paris-Saclay

4 avenue des Sciences
91 190 Gif-sur-Yvette

Coordonnées GPS

Entrer dans son GPS : Rue Yvette Cauchois

- Latitude Nord : 48° 42' 47.318
- Longitude Est : 2° 9' 43.715
- Latitude : 48.713144
- Longitude : 2.162143

En transport en commun depuis Paris

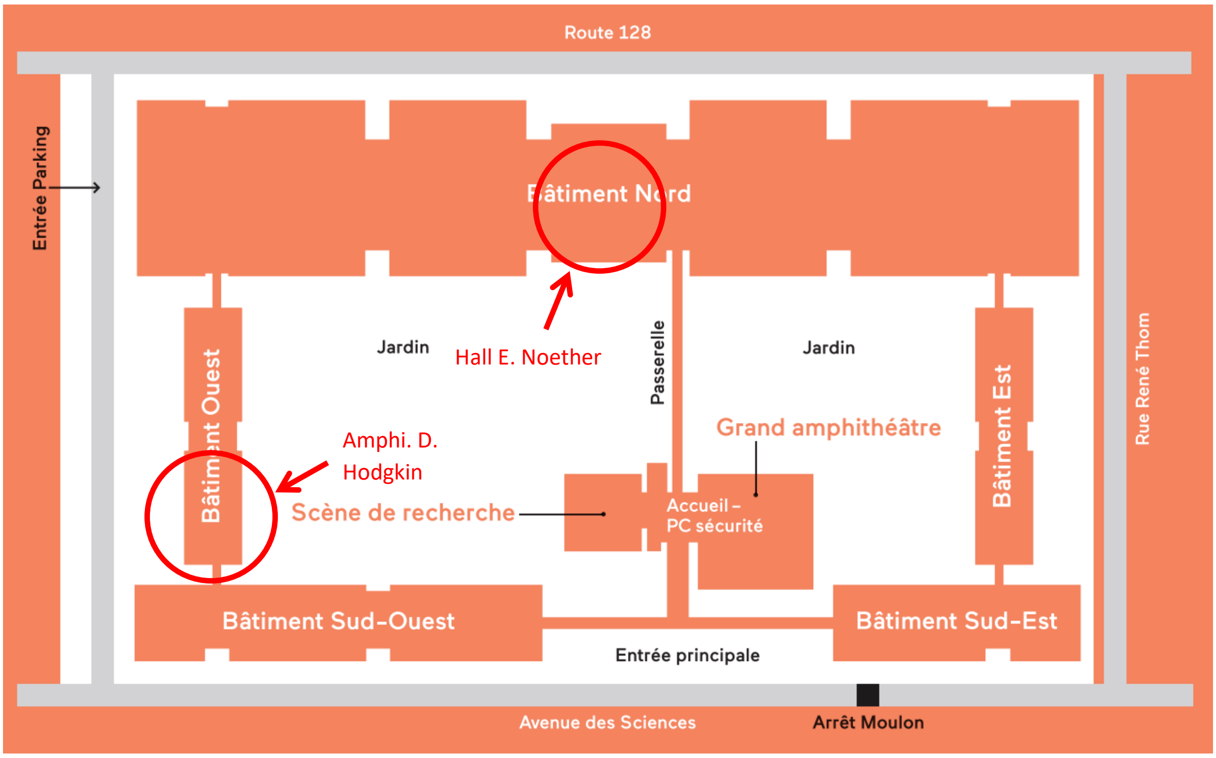
RER B (Saint-Rémy-lès-Chevreuse) ou RER C (Massy-Palaiseau)
Arrêt : « Massy-Palaiseau »
Puis prendre un des bus suivants :
- Bus 91.06 (Christ de Saclay)
- Bus 91.10 (Saclay)
Arrêt : « Moulon » (20 minutes depuis la gare).

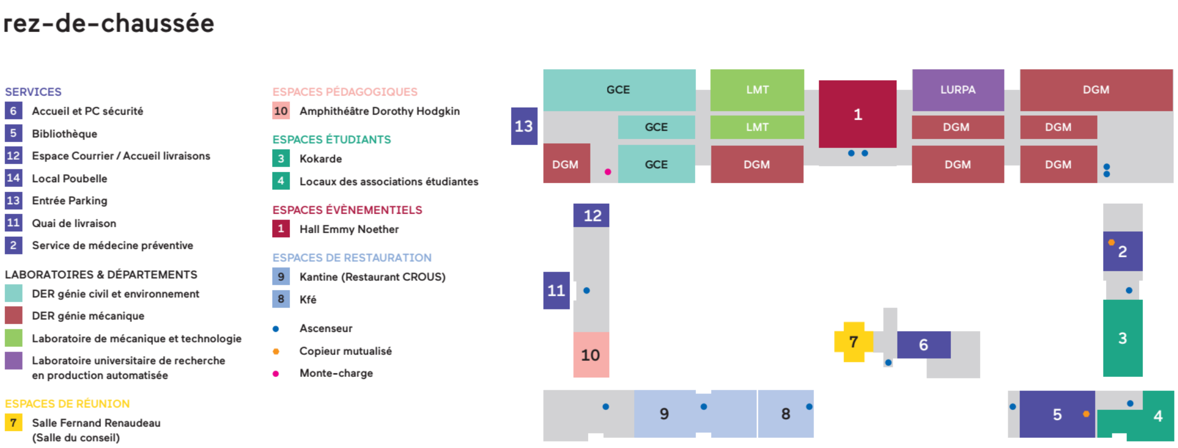
OU

RER B (Saint-Rémy-lès-Chevreuse)
Arrêt : « Le Guichet »
Puis prendre le bus suivant :
- Bus 9 (Christ de Saclay)
Arrêt : « Moulon » (5/10 minutes depuis la gare).

Plan de l'ENS Paris-Saclay

Les journées SP2P'22 se dérouleront dans l'amphithéâtre Dorothy Hodgkin (bâtiment Ouest, RDC). Les sessions posters, les pauses-café ainsi que le cocktail dînatoire auront lieu dans le hall Emmy Noether (bâtiment Nord, RDC)





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Journées Annuelles SP2P'2022

Programme scientifique – 7-8 Juin 2022

ENS Paris-Saclay – Amphithéâtre Dorothy Hodgkin – 4 avenue des Sciences, 91190 Gif sur Yvette

Mardi 7 Juin

13:00 – 13:10	**Introduction** (accueil dès 12:30)
13:10 – 13:50	**Keynote** – **Michael Oelgemöller** – Fresenius Univ. Applied Science (Germany) *"Green chemistry with light – from lab-scale photochemistry to the solar production of chemicals and continuous-flow photochemical synthesis"*
13:50 – 14:10	**Stéphane Rigaut** – Univ. Rennes *"Photo-control of NIR emission"*
14:10 – 14:30	**Aurélie Djian** – ENS Paris-Saclay *"Highlighting photophysical properties of a new negative photochromic class"*
14:30 – 14:45	**Pause**
14:45 – 15:05	**Aude Bouchet** – Univ. Lille *"A new tool for time-resolved hyperspectral nano-imaging of up-converting nanoparticles"*
15:05 – 15:25	**Zhouyun Chen** – Univ. Clermont Auvergne *"The association between polycarbonate photoageing and oxygen permeability"*
15:25 – 16:25	**Session posters**
16:25 – 16:55	**Invitée** – **Marie-Claire Schanne-Klein** – École Polytechnique *"Structural imaging of collagen in biological tissues using Second Harmonic Generation microscopy"*
16:55 – 17:15	**Mario Andrés Gomez Fernandez** – Univ. Reims Champagne-Ardenne *"Application of the Paternò-Büchi reaction to the synthesis of novel fluorinated scaffolds"*
17:15 – 17:35	**Anam Fatima** – Univ. Paris-Saclay *"Tracing the photo-driven electron transfer efficiency between octahedral molybdenum halide cluster* $[Mo_6I_8Cl_6]^{2-}$ *and different polyoxometalates"*
17:35 – 17:50	**Pause**
17:50 – 18:10	**Eva Pugliese** – Univ. Paris-Saclay *"Light-induced* CO_2 *reduction catalysis with urea-modified iron porphyrin"*
18:10 – 18:30	**Robert Pansu** – ENS Paris-Saclay *"De l'analyse des déclins de luminescence en phase solide"*
18:30 – 19:15	**Hommage au professeur Jean Faure (1935-2017)**
19:15 – 22:00	**Cocktail dînatoire**

Mercredi 8 Juin

09:00 – 09:20	**Cassandre Quinton** – Univ. Rennes *“[4]-Cyclo-2,7-carbazole as host material in high-efficiency red phosphorescent OLEDs: a new perspective for molecular nanohoops in organic electronics”*
09:20 – 09:40	**Émilie Renouard** – ENS PSL *“Time-resolved spectroscopic study of the ON → OFF photoswitching reaction pathway of the fluorescent protein Dreiklang”*
09:40 – 10:10	**Invité** – **Guillaume Schull** – Univ. Strasbourg *“From single-molecule fluorescence to photosynthesis with an STM”*
10:10 – 10:30	**Auriane Perrin** – École Polytechnique *“Photo-control of G-quadruplexes folding and unfolding with azobenzene derivatives”*
10:30 – 11:15	**Session posters**
11:15 – 11:35	**Philipp Gotico** – CEA, Univ. Paris-Saclay *“The curious case of a Ru-Fe sensitizer-catalyst dyad for CO_2 reduction”*
11:35 – 11:55	**Céline Molinaro** – Univ. Haute Alsace *“Thermopolymerization induced through the plasmonic excitation of gold nanoparticles”*
11:55 – 12:15	**Minh-Huong Ha-Thi** – Univ. Paris-Saclay *“Broadband light-absorbing BODIPY-C60-distyryl BODIPY triad as heavy-atom-free organic triplet photosensitizers”*
12:15 – 13:00	**Visite du laboratoire PPSM**
13:00 – 14:00	**Déjeuner**
14:00 – 14:30	**Invitée** – **Aurélie Perrier** – Univ. Paris Cité / Univ. PSL *“Photoinduced processes under constraints: a theoretical insight”*
14:30 – 14:50	**Jonathan Piard** – ENS Paris-Saclay *“Universal buffer: a powerful tool to investigate the impact of pH on photophysical and (photo)chemical properties from pH 1.9 to 12”*
14:50 – 15:10	**Valéria Lepère** – Univ. Paris-Saclay *“Conformation isomerism of 1–indanol probe by PhotoElectron Circular Dichroism”*
15:10 – 15:30	**Jean-Sébastien Lauret** – ENS Paris-Saclay *“Investigation of the optical properties of single nanographene”*
15:30 – 16:00	**Conclusion – Remise des prix**

Hommage au professeur Jean Faure (1935-2017)

Lors des Journées Annuelles SP2P'2022, nous rendrons un hommage au professeur Jean Faure.

Photophysicien de renommée internationale, Jean Faure a commencé sa carrière de chercheur à l'Université de Bordeaux, au laboratoire de photophysique moléculaire. Sur le plan scientifique, il est le « fils de Jacques Joussot-Dubien, petit-fils d'Adolphe Pacault et arrière-petit-fils de Paul Pascal », et nous bénéficions à notre tour de ses réalisations, à présent.

Jean Faure a grandement contribué à développer et à structurer la photochimie française, à la fois scientifiquement et politiquement. Nous lui devons l'émergence de deux centres importants dans le domaine : il a fondé et dirigé le Laboratoire de Photochimie Générale à Mulhouse dans les années 1970 et le Laboratoire de Photophysique et de Photochimie Supramoléculaires et Macromoléculaires (PPSM) à Cachan deux décennies plus tard. Il a également dirigé le prestigieux Laboratoire de Physico-Chimie des Rayonnements de l'Université Paris-Sud (actuellement Université Paris-Saclay) dans les années 1980, avant d'exercer des responsabilités de haut niveau au Ministère de la Recherche et à l'ENS Cachan (Direction scientifique).

Toujours à l'affût des progrès technologiques, il a acquis le premier laser Quantel, le premier laser titane saphir de Spectra Physics et contribué au développement de lasers avec BMI. Une de ses actions, représentative de ses liens forts avec les entreprises, a été la création et l'animation du Club EDF de photochimie, véritable groupe de travail réunissant d'importants acteurs du monde académique et industriel.

Les débuts du PPSM

Extrait de l'histoire du PPSM
Présentée en 2019 lors de l'exposition « Une école normale supérieure à Cachan : 1956-2020 »

Nommé Professeur de Chimie à l'ENS Cachan en 1988, Jean Faure, photochimiste et professeur de chimie à l'Université Paris-Sud, avait reçu du directeur de l'ENS de l'époque, le Professeur Yves Malier, la mission de créer un laboratoire de recherche en chimie pouvant avoir à terme une reconnaissance internationale. Initialement, l'équipe de Cachan était constituée, outre son responsable, d'une technicienne chimiste, Marie-Claude Vernières et de deux chercheurs CNRS : Jean-Pierre Galaup, photophysicien et Claude Bied-Charreton, chimiste des porphyrines. Dès le début, on peut noter cette ambivalence de l'équipe : un axe en chimie de synthèse, et un autre dans un domaine lié à l'optique. Dès 1990, Jean Faure obtient la reconnaissance de ce groupe de chercheurs comme « Jeune Équipe ». En 1993 des membres de l'équipe de Jean Faure à Orsay - Jacques Delaire, professeur, Keitaro Nakatani et Robert Pansu, chargés de recherche CNRS, tous les trois photochimistes - rejoignent l'équipe de Cachan. Celle-ci, devenue le Laboratoire de Photophysique et Photochimie Moléculaire (LPPM) est reconnue comme unité associée au CNRS en 1995 (URA 1906). La nouvelle unité s'est vue renforcée par une équipe du Conservatoire National des Arts et Métiers (CNAM) de Paris, l'équipe des professeurs Bernard Valeur et Élisabeth Bardez, spécialistes de la fluorescence appliquée aux capteurs d'ions métalliques.

Ce petit laboratoire intégrera ensuite de nombreux autres ingénieurs, techniciens, chercheurs et enseignants-chercheurs, pour donner le laboratoire de Photophysique et de Photochimie Supramoléculaires et Macromoléculaires (PPSM) tel que nous le connaissons aujourd'hui.

Témoignant d'une ouverture d'esprit visionnaire, Jean Faure mettait en pratique l'interdisciplinarité et l'international à une époque où ces mots étaient très peu dans les esprits. Sachant « parler de chimie aux physiciens et de physique aux chimistes », il a été à l'origine de la création d'une plateforme interdisciplinaire à l'ENS Cachan, entre le PPSM et le LESIR (Laboratoire d'Électricité, des Signaux et de Robotique), actuellement le laboratoire SATIE (Systèmes et Applications des Technologies de l'Information et de l'Énergie). Son aura et ses connexions internationales ont également permis aux laboratoires qu'il a créés de susciter l'intérêt de grands scientifiques du domaine et d'être intégré rapidement dans la communauté internationale, entraînant jeunes chercheurs et d'étudiants dans ces échanges.

Jean Faure à Mulhouse. Sa passion pour les chevaux n'était pas un secret pour ses collègues. (Photo fournie par Sylvain Faure)

La tenue des Journées Annuelles SP2P'2022 à l'ENS Paris-Saclay, dans les nouveaux locaux hébergeant le PPSM, dont Jean Faure est le directeur-fondateur, est l'occasion d'évoquer son souvenir. Après la projection d'une vidéo réalisée par son fils, Sylvain, sur le thème du cheval, une passion partagée avec son père, des anciens collègues et élèves apporteront un témoignage sur les souvenirs les plus marquants et sur l'héritage scientifique de Jean Faure.

RESUMES

Keynote

Et

Conférences invitées

Green Chemistry with Light – From Lab-scale Photochemistry to the Solar Production of Chemicals and Continuous-Flow Photochemical Synthesis

Michael Oelgemöller[1]

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Email: michael.oelgemoeller@hs-fresenius.de

Common drawbacks of photochemistry are the necessity to use hazardous solvents, energy-intensive artificial light sources or high dilutions. Over the last decades we have developed photodecarboxylations as an efficient access to macrocycles or addition products. Due to the high water-solubility of the starting carboxylates, these reactions can be conducted in aqueous solutions. Large-scale syntheses (<50 g) have also been realised using novel falling-film or circulating loop reactors. The reaction has been furthermore used as a key-step in the synthesis of biologically active target compounds [1]. To overcome the high energy demand of artificial light sources, natural sunlight can be used as a 'free' light source for the production of chemicals [2]. We have realized a number of laboratory- to large-scale solarchemical reactions in direct sunlight. All reactions utilized biomass-derived starting materials and gave complete conversions and excellent yields after short illumination times. The combination of microspace and flow operation is especially advantageous for photochemical transformations. We have thus studied a series of photoreactions under continuous-flow conditions. In all cases examined, the flow reactions gave higher conversions or yields and better product qualities. We have also developed photochemical-thermal tandem processes for multi-step reactions to bioactive compounds *in series* [3]. Parallel photochemical operations have also been conducted in a multicapillary flow reactor and solar exposures in a concentrating trough reactor. Recently, we became also interested in the production of biodiesel through photocatalysis.

Figure 1. Loop reactor, solar CPC-reactor and photochemical-thermal tandem flow-reactor.

[1] S. Mumtaz, M. J. Robertson, M. Oelgemöller *Aust. J. Chem.* **2018**, *71*, 634–648.

[2] J. S. Wau, M. J. Robertson, M. Oelgemöller *Molecules* **2021**, *26*, #1685.

[3] S. Mumtaz, M. J. Robertson, M. Oelgemöller *Molecules* **2019**, *24*, #4527.

Structural imaging of collagen in biological tissues using Second Harmonic Generation microscopy

Margaux Schmeltz[1], Clothilde Raoux[1], Gaël Latour[1,2], Marie-Claire Schanne-Klein[1]

[1] *Laboratoire d'Optique et Biosciences, CNRS, Inserm, Ecole Polytechnique-IP Paris, Palaiseau*
[2] *Université Paris-Saclay, Gif-Sur-Yvette, France*
Email: marie-claire.schanne-klein@polytechnique.edu

Second harmonic generation (SHG) microscopy is the gold standard technique for collagen imaging without any labeling and with an unmatched sensitivity and specificity in intact tissues [1]. Collagen is a major component of connective tissues such as arteries, skin, bones and cornea. It is characterized by a 3D multiscale structure that is a key distinctive feature of every tissue and governs its functional behavior. A defective collagen 3D structure leads to tissue malfunctions, which is the case in many diseases featuring tissue remodeling. 3D imaging of collagen is therefore a major biomedical concern to decipher the relationship between structure and function in tissues and to implement sensitive and reliable diagnosis of diseases affecting collagen structure.

Analysis of collagen SHG images is however a complicated issue because SHG is a coherent optical signal and because biological tissues exhibit complex and often heterogeneous structures. In this context, we have implemented polarization-resolved SHG imaging, which provides the mean orientation of collagen fibrils in the imaging plane as well as their degree of orientational disorder [2, 3]. The normalized difference of SHG signals excited with left and right circular polarizations (that is SHG circular dichroism), on the other hand, specifically visualizes collagen fibrils oriented out of the imaging plane and probes their degree of polarity [3]. These advanced SHG modalities are efficient tools for quantitative structural imaging of collagen-rich tissues.

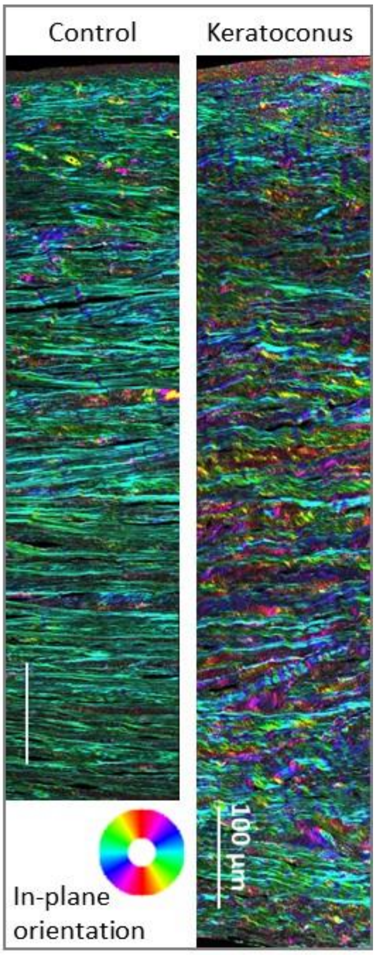

***Figure 1**: polarization-resolved SHG imaging of histological sections of healthy and pathological Human corneas (from [2]).*

[1] S. Bancelin et al, *Nat. Commun.*, **2014**, *5,* 4920.
[2] C. Raoux et al, *Biomed. Opt. Express,* **2021**, *12(7),* 4163-4178.
[3] M. Schmeltz et al, *Sci. Adv.,* **2021**, *7(29),* eabg1090.
[4] M. Schmeltz et al, *Optica* **2020**, *7(11),* 1469-1476.

From single-molecule fluorescence to photosynthesis with an STM

S. Cao[1], A. Roslawska[1], B. Doppagne[1], M. Roméo[1], M. Féron[2], F. Chérioux[2], H. Bulou[1], F. Scheurer[1], G. Schull[1]

[1] *Université de Strasbourg, CNRS, IPCMS, UMR 7504, Strasbourg, France*
[2] *Université Bourgogne Franche-Comté, FEMTO-ST, UFC, CNRS, Besançon, France*
Email: schull@unistra.fr

The electric current traversing the junction of a scanning tunneling microscope (STM) may lead to a local emission of light that can be used to generate sub-molecularly resolved fluorescence maps of individual molecules. Combined with spectral selection and time-correlated measurements, this hyper-resolved fluorescence microscopy approach allowed us to scrutinize the vibronic structure of individual molecules [1] in a very similar way than in the recent TERS reports, without requiring an optical excitation. We used this approach to characterize the photonics properties of charged species [2], to track the motion of hydrogen atoms within free-based phthalocyanine molecules [3], and more recently to follow resonance energy transfers between individual pigments, exploring processes occurring in photosynthetic complexes with sub-molecular spatial resolution [4].

These results constitute an important step towards photonic measurements with atoms-scale resolution [5].

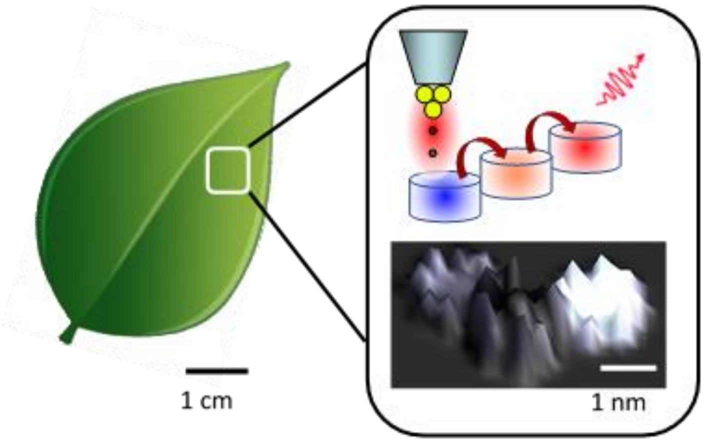

Figure 1. Exploring energy transfers occurring in leafs with a scanning tunneling microscope.

[1] B. Doppagne et al., Phys. Rev. Lett. 118, 127401 (2017)

[2] B. Doppagne et al. Science 361, 251 (2018)

[3] B. Doppagne et al. Nature Nanotechnol.15, 207 (2020).

[4] S. Cao et al. Nature Chem. 12, 766 (2021)

[5] A. Roslawska et al. Physical Review X 12, 011012 (2022)

Photoinduced processes under constraints: a theoretical insight.

Laura Le Bras,[1] **Laure Jourdain de Thieulloy,**[1] **Aurélie Perrier**[1,2]

[1] *Institute of Chemistry for Life and Health Sciences (i-CLeHS), Chimie ParisTech, PSL Research University, CNRS, F-75005 Paris, France*

[2] *Université Paris Cité, F-75006 Paris, France*

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Controlling the optical properties of materials is a considerable challenge for high-tech applications. In addition to the choice of efficient molecules (capable of absorbing or emitting in a particular region of the spectrum with high efficiency), it is important to consider the effect of the environment (solution, aggregate, crystalline environment, or polymer matrix) on the targeted properties. We therefore propose to rationalize the interactions that can exist between photo-induced processes (absorption, emission, photochemical reactions) and the environment, with the help of theoretical models based on quantum chemistry (DFT and TD-DFT calculations) and molecular modeling (classical molecular dynamics). In this presentation, we will first be interested in the modelling and the rationalization of the aggregation-induced emission (AIE) and crystallization-induced emission (CIE) photophysical phenomena. [1-4] Then, we will be interested in the properties of photonastic systems. These materials can convert light energy into mechanical energy and are the subject of pre-determined and repeatable deformations in response to light stimuli. This phenomenon is usually associated with plants and flowers, whose petals open in the daylight and close in the evening in response to a light stimulus. Among these materials, light-responsive polymers, composed of photochromic molecules embedded in a polymer matrix, are of high interest and have been recently proposed for a wide range of applications in microfluidics, biomedics, soft robotics and motors. After presenting the tailored computational protocol that we have developed to propose a realistic description of these systems, we will discuss (i) the impact of the polymer matrix on the photochromic properties of the photoswitch and (ii) the impact of the photochromic reaction on the polymer environment. [5]

[1] L. Le Bras, C. Adamo, A. Perrier, *J. Phys. Chem. C,* **2017**, 25603–25616.

[2] L. Le Bras, K. Chaitou, S. Aloïse, C. Adamo, A. Perrier, *Phys. Chem. Chem. Phys.*, **2019**, 46-56

[3] L. Le Bras, C. Adamo, A. Perrier, *ChemPhotoChem,* **2019**, 794-803.

[4] L. de Thieulloy, L. Le Bras*, B. Zumer, J. Sanz Garcia, C. Lemarchand, N. Pineau, C. Adamo, A. Perrier, *ChemPhysChem***, 2021**, 1802

[5] L. Le Bras, C. Lemarchand, S. Aloïse, C. Adamo, N. Pineau, A. Perrier, *J. Chem. Theory Comput.* **2020,** 11, 7017–7032

RESUMES

Communications Orales

Photo-Control of NIR Emission

Hassan Al Sabea,^{1} Lucie Norel,^{1} Olivier Galangau,^{1} Olivier Maury,^{2} François Riobé,^{2} Stéphane Rigaut^1

^{1} *Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes UMR 6226, F-35000 Rennes, France*
^{2} *Univ. Lyon, CNRS, ENS Lyon, Laboratoire de Chimie UMR 5182 46 allée d'Italie, F-69007 Lyon, France*

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Lanthanide ion complexes display unique long-lived and narrow bandwidth luminescence ranging from the visible up to the near infra-red spectral ranges. Hence, they led to wide applications in material chemistry and biological imaging. Remote control of this luminescence is now an attractive target for the development of more elaborated optical materials.

For this purpose, our group recently focused on the development of photochromic lanthanide complexes, with a special interest in the NIR emitting ytterbium(III) ion since it is much less studied than the red emitting europium(III) ion. In particular, we achieved a photochromic β-diketonate ligand having a dithienylethene unit that is very efficient for the switching ON and OFF of ytterbium(III) luminescence. This system presents a dynamic response which behavior can be transferred to polymer films. We also developed a related complex displaying an additional antenna allowing non-destructive read-out and redox-switching.

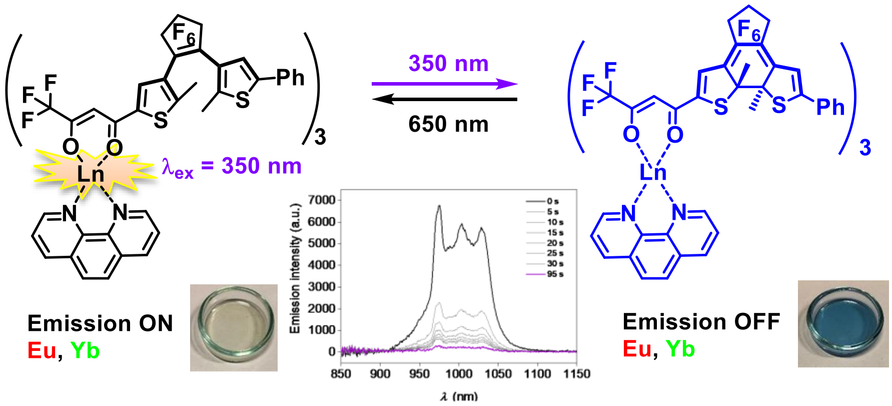

Figure 1. NIR emission photocontrol.

[1] L. Norel, O. Galangau, H. Al Sabea, S. Rigaut, *ChemPhotoChem* **2021**, *5*, 393-405

[2] H. Al Sabea, L. Norel, O. Galangau, T. Roisnel, O. Maury, F. Riobé, S. Rigaut, *Adv. Funct. Mater.* **2020**, 30, 2002943

[3] H. Al Sabea, L. Norel, O. Galangau, H. Hijazi, R. Métivier, T. Roisnel, O. Maury, C. Bucher, F. Riobé, S. Rigaut, *J. Am. Chem. Soc.* **2019**, *141*, 20026-20030

Highlighting photophysical properties of a new negative photochromic class

<u>Aurélie Djian</u>,[1] **Adèle Laurent**[2]**, Guillaume Laurent,**[1] **Keitaro Nakatani,**[1] **Joanne Xie,**[1] **Rémi Métivier**[1]

[1] *Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, 91190 Gif-sur-Yvette, France*
[2] *Université de Nantes, CNRS, CEISAM, 44322 Nantes, France*
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Various “negative”* photochromic molecules have been recently studied, compared to “positive” photochromes, and they have already proved to be interesting for various applications (security devices, biological probes or drugs, solar energy storage etc).[1], [2] A new negative photochromic family, based on nitrile-rich acceptors (**NRA**), have gained attention these past few years due to their attractive properties.[3] Nevertheless, their photophysical properties remain relatively unexplored.

In this work, we investigate the behavior of NRA compounds in different conditions. First, the synthesis and spectroscopic properties of a series of three NRA-based photochromic molecules are described. By studying the influence of solvent, temperature and pH[4] on their photophysical and photochemical properties, we show that absorption, fluorescence and photoswitching kinetics can be drastically tuned (Figure 1). Nanosecond transient absorption and DFT calculations provide useful information to understand these specific behaviors.

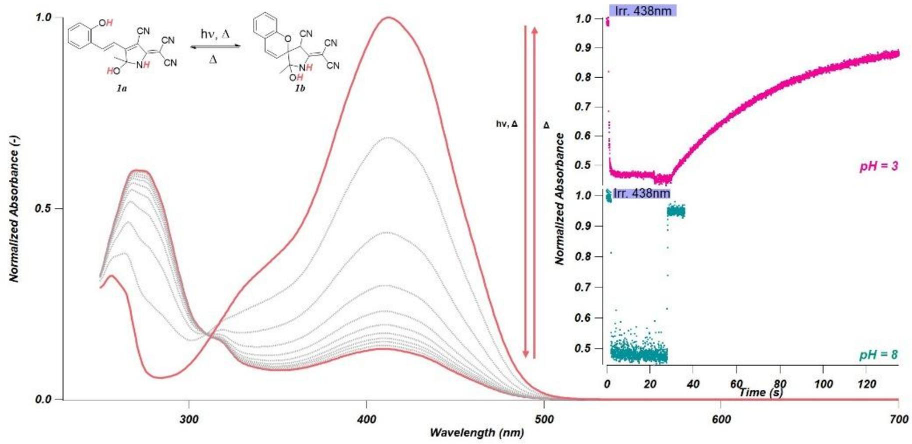

Figure 1. (Left) Absorption spectra of molecule **1** collected during an irradiation at 438 nm, in CH_3CN. (Right) Absorbance at 430 nm of molecule **1** followed during an irradiation at 438 nm (35.5 mW), in a CH_3CN:H_2O medium at 2 different pH (**1**a: colored form, **1**b: colorless form).

* Contrarily to “positive” photochromes, the colored form is the stable isomer in “negative” ones.

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A new tool for time-resolved hyperspectral nano-imaging of up-converting nanoparticles

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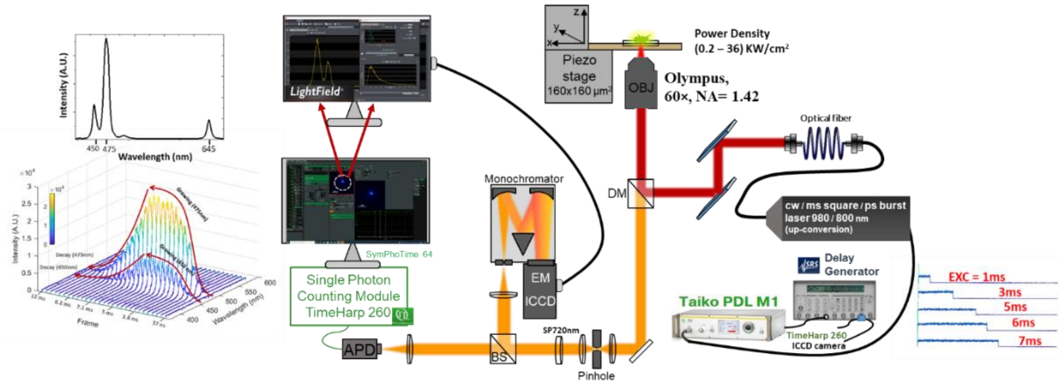
Up-conversion nanoparticles are lanthanide-doped nanoparticles which present the unique feature of being able to emit light up to the blue region of the visible spectrum while being excited by near infrared light. Hence, they represent very attractive probes for bio-imaging because of the absence of autofluorescence and a great penetration depth into tissues. They can also be used to design new photonics materials[1] with specific spatial nano-organization. Having a hyperspectral nano-imaging method to record spatially resolved spectra and emission lifetimes for different UCNP nano-organizations, from single UCNP to 3D clusters, would allow to probe the intra and inter-particle up-conversion dynamics controlling their emission properties. However, the long lifetime of these systems prevents from using classical fluorescence lifetime imaging microscopes (FLIM). We have thus developed a new confocal microscope based on a millisecond-square pulse NIR excitation and an intensified gated CCD camera in order to measure space- and time-resolved spectra. We will discuss here two applications of this new tool: (i) we first investigated the emission properties of Tm- and Er-based core and core-shell UCNP 2D layer. According to the nanometric spatial arrangement of the particles, we could demonstrate that the emission dynamics of single particles, 2D monolayer or 3D aggregates differ in terms of power-dependent emission band ratios and lifetimes. (ii) We studied the energy transfer dynamics of single UCNP to organic dyes films. We could follow the transfer of the exciton from UCNPs to organic dye in the vicinity and its diffusion within the film.



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The association between polycarbonate photoageing and oxygen permeability

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Abstract:

Polycarbonate (PC) is an amorphous thermoplastic polymer which is used in several applications such as CD protection. As a material, PC may be photodegraded through an oxidative chain radical process. This leads to a change of its optical, mechanical and barrier properties [1]. Despite the importance of the latter in various uses, the effect of photooxidation on oxygen permeability has been scarcely reported so far, and this work aims to relate photoageing and change in oxygen transport properties for PC.

Permeation coefficient for oxygen in PC films were obtained upon UV light exposure in relation with photoageing kinetics (Figure 1). The clear decrease of this parameter shows that photoinduced cross-linking is likely involved. This conclusion was further strengthened by micro-hardness and gel fraction experiments. Moreover, the effect of sequential photoageing of the PC films (on one side first, then on the other side) on the permeability process is reported and discussed.

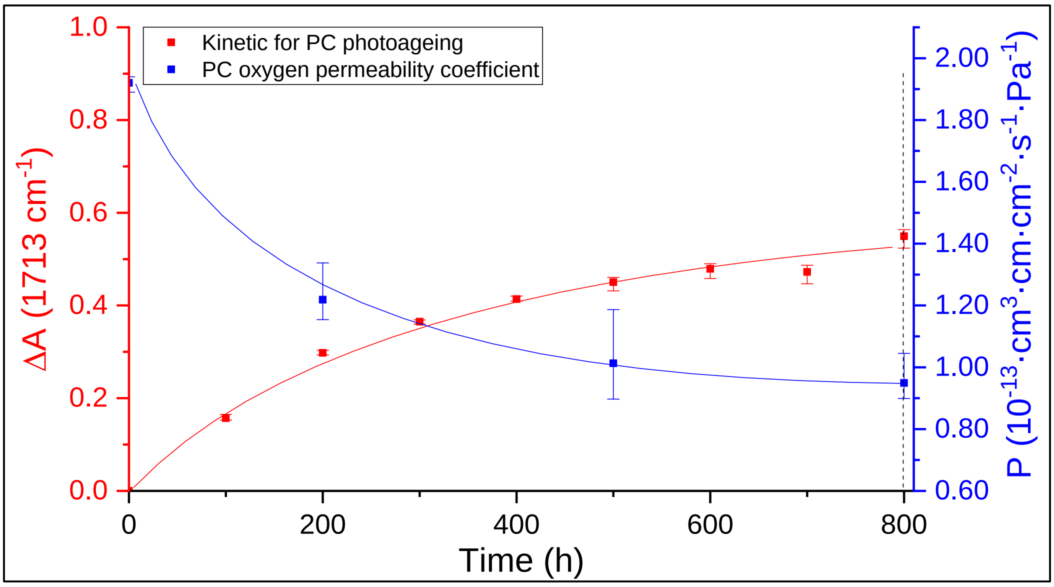

Figure 1: *Oxygen permeation coefficient and the absorbance change at 1713 cm^{-1} upon PC photoageing*

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Application of the Paternò-Büchi Reaction to the Synthesis of Novel Fluorinated Scaffolds.

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Keywords: Cycloaddition, Fluorinated scaffolds, heterocycles, photochemistry, reaction mechanisms.

Photochemical reactions are extensively applied to organic synthesis [1,2]. In recent years, photochemical reactions have become a common tool in modern organic chemistry laboratories since they enrich the chemical space available at the ground state, for example in the search for biological active molecules [1,2,3].

The Paternò-Büchi reaction is a [2+2] photocycloaddition between an electronically excited carbonyl compound and an alkene, leading to oxetanes [4]. Despite the fact that this reaction is one of the most extensively researched organic photochemical reactions (mechanism, regio-, stereo- selectivities) little is known about the use of heteroaromatic ketone partners for this photocycloaddition. In the context of the search for biological activity, we investigated the application of the Paternò-Büchi reaction to the synthesis of new scaffolds using simple and inexpensive ketones and olefins [5]. In this communication, we present our recent results concerning the Paternò-Büchi reaction using benzoyl pyridines and furan as the olefin partner.

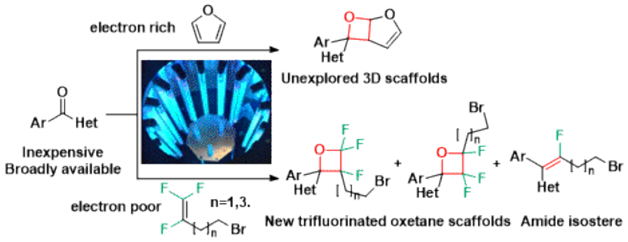

Figure 1: Application of the Paternò-Büchi reaction using heteroaromatic ketones, electron rich and electron poor olefins.

In parallel studies, the reactivity of aromatic and heteroaromatic ketones with fluorinated olefins was investigated in detail (Figure 1). The stability of the fluorinated oxetane product depends on the substitution of the aromatic ring. A subsequent methathesis-like reaction (photo-Wittig reaction) yields amide isosteres.

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Tracing the photo-driven electron transfer efficiency between octahedral molybdenum halide cluster $[Mo_6I_8Cl_6]^{2-}$ and different polyoxometalates

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The quest for photochemical energy storage has enabled appreciable interest in the study of electron transfer properties in transition metal complexes. The long-lived triplet state of coordination complexes enables efficient electron transfer making them promising for solar energy storage.**[1,2]** In particular, octahedral metal halide clusters represent a class of electron rich species known for their intense luminescence and considerably long-lived triplet state.**[3]** On the other side, polyoxometalates (POMs) correspond to molecular ‘electron reservoir” built from group VI transition-metal centers in their highest oxidation state (Mo^{VI} and W^{VI}) assembled together with oxygen atoms within a wide variety of structures and compositions .**[4]** Incorporating the advantage of their complementary properties present an attractive way to further the electron transfer studies on these all-inorganic chemical systems.

In our work, photophysical characterization (steady state and nanosecond scale time-resolved spectroscopy) of the molybdenum halide cluster $[Mo_6I_8Cl_6]^{2-}$; acting as photosensitizer in combination with different POMs: $[PW_{12}O_{40}]^{3-}$, $[PW_{11}VO_{40}]^{4-}$, $[P_2W_{18}O_{62}]^{6-}$ and $(BW_{12}0_{40})^{5-}$; acting as catalytic platform has been presented. The work highlights a novel study on the photoinduced electron transfer process between the two entities (Figure) and explores the dependence of electron transfer efficiency on the charge density of the metal atom of the POM, leading up to exploring their potential in clean energy production.

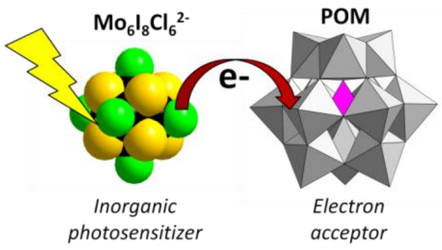

Figure: Photo-induced electron transfer from $[Mo_6I_8Cl_6]^{2-}$ to polyoxometalate

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Light-induced CO_2 reduction catalysis with urea-modified iron porphyrin

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Finding ways to valorize and transform CO_2 into fuel using renewable energies as an alternative to fossil fuels is crucial in the current scientific research. A possible approach is electro or light induced molecular catalysis. Iron porphyrins had been reported to be active catalysts for CO_2 electroreduction since the 80s[1]. Our group has previously developed a highly active iron porphyrin catalyst bearing urea groups in the second coordination sphere (**UrFe**)[2]. The use of the urea scaffold to stabilize the CO_2 adduct enabled the catalyst to display low overpotentials and high turnover frequency. These results lead us to investigate its catalytic activity in a light induced catalytic system. When using ruthenium tris-bipyridine as a photosensitizer, our study shows that the second coordination sphere effect can also be transposed to homogeneous photocatalysis for CO_2 reduction. Careful tuning of the photocatalytic reaction parameters and modification of second coordination sphere led to a great enhancement of catalyst durability, with one of the highest turnover numbers (TON>7000) reported in the literature, and excellent selectivity for CO (>99%)[3].

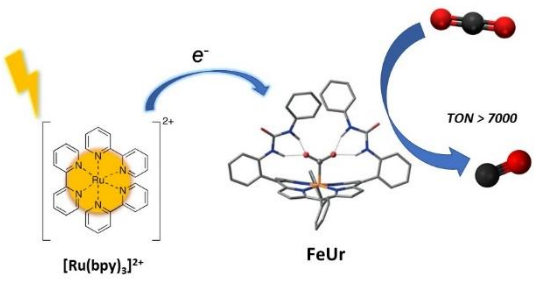

Figure 1. Simplified scheme of CO_2-to-CO photocatalytic reduction using $[Ru(bpy)_3]^{2+}$ as photosensitiser and FeUr as catalyst.

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De l’analyse des déclins de luminescence en phase solide

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

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

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

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

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

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

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

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

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[4]-Cyclo-2,7-carbazole as host material in high-efficiency red Phosphorescent OLEDs: A new perspective for molecular nanohoops in organic electronics

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In the last ten years, the development of π-conjugated nanohoops has been considerable owing to their remarkable properties.[1] However, to date, their incorporation in organic electronic devices remains very scarce.[2] In this work, we report the first incorporation of a nanohoop, namely [4]-Cyclo-*N*-butyl-2,7-carbazole **[4]C-Bu-Cbz**, as host material in a high performance Phosphorescent Organic Light-Emitting Diode (PhOLED). Using the red phosphor Ir(MDQ)$_2$(acac), the **[4]C-Bu-Cbz**-based PhOLED displays a very high External Quantum Efficiency (EQE) of 17.0 %, a Current Efficiency (CE) of 20.6 Cd/A and a Power Efficiency (PE) of 25.8 lm/W. This performance is significantly higher than that of its linear counterpart, *N*-butyl-2,7-quartercarbazole **[4]L-Bu-Cbz**, which displays an EQE of 11.1 %, a CE of 13.0 cd.A^{-1} and a PE of 15.7 lm/W. This study, which includes emission, electrochemical, morphological and charge transport properties, shows that the best performances of **[4]C-Bu-Cbz** arises from (i) quicker radiative deactivation processes of the phosphorescent dopant in the emissive layer (EML), (ii) better transporting properties and (iii) higher homogeneity of the EML. Thus, nanohoops can be efficiently used as organic semi-conductors in electronics and opens the way to their practical uses in high-performance optoelectronic devices, which is now the next stage of their evolution.

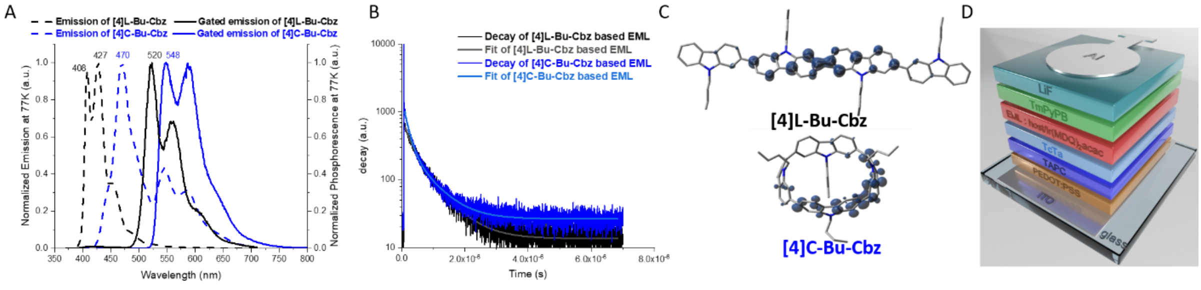

Figure 1. (A) Normalized emission at 77 K**;** (B) time resolved photoluminescence; (C) Triplet Spin Density distribution and (D) Schematic representation of the PhOLED.

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Time-Resolved Spectroscopic Study of the ON → OFF Photoswitching Reaction Pathway of the Fluorescent Protein Dreiklang

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Reversibly switchable fluorescent proteins (RSFPs) are able to switch reversibly between a fluorescent ON state and a non-fluorescent OFF state. Of particular interest for advanced imaging, their use is in most cases hindered because excitation of the fluorescent ON form simultaneously triggers the decay of the ON population. Dreiklang is one of the rare RSFPs, whose photophysics is fully decoupled: three different excitation wavelengths respectively lead to ON→OFF photoswitching, OFF→ON photoswitching and fluorescence emission. This property is explained by a unique photoswitching mechanism based on hydration/dehydration of the chromophore (Figure 1) [1]. However, the nature and kinetics of the involved elementary steps are still poorly known. We present here the first transient absorption spectroscopy experiments on Dreiklang ON-state. Different setups were used to access relevant timescales from 100 fs to milliseconds and disclosed OFF formation within 30 ns (Figure 2) [2]. Comparison of the photoswitching properties and dynamics of four single-point variants of Dreiklang plus recent theoretical studies brought insights into the role of neighboring amino acids in the mechanism and enabled us to entangle ON → OFF photoswitching from side reaction pathways [3],[4].

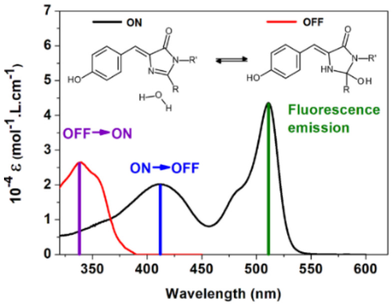

Figure 1. Absorption spectra of Dreiklang

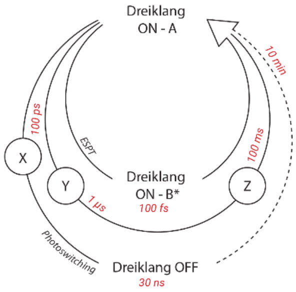

Figure 2. Photoinduced reactions on Dreiklang

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Photo-control of G-quadruplexes folding and unfolding with azobenzene derivatives

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G-quadruplexes are DNA secondary structures formed by guanine-rich sequences, which self-assembles into stacks of guanine tetrads. These structures exhibit a large variety of topologies, the folding/unfolding of which has been proven to be involved in numerous key-biological processes, such as DNA transcription, replication or repairment.[1] It has also been shown that these processes can be induced by the photoisomerization of cationic photoswitches interacting with DNA.[2,3] In this context, we undertook a study of the folding dynamics of several G-quadruplex-forming sequences interacting with AZO, a cationic azobenzene derivative. I will present the characterization of different complexes formed by AZO and several short G-quadruplex sequences by various techniques, such as UV-visible absorption, circular dichroism, which is particularly adapted to the study of these biological structures, NMR and femtosecond transient absorption. We now plan to study their folding/unfolding dynamics by time-resolved circular dichroism spectroscopy over an extended time scale from a few picoseconds to a few seconds.[4]

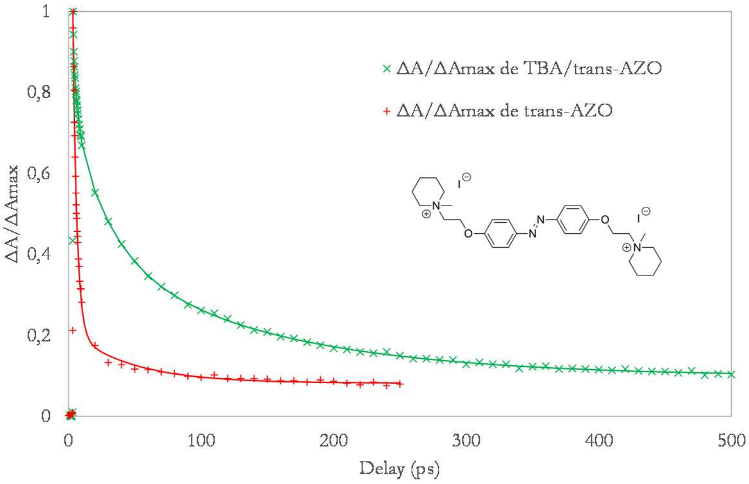

Figure 1. Transient absorption of AZO measured in aqueous solution (10mM Tris) at 520 nm after irradiation at 400 nm in presence or absence of the G-quadruplex sequence TBA (5'-(TGG TGG TGT GGT GGT)-3').

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The curious case of a Ru-Fe sensitizer-catalyst dyad for CO_2 reduction

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Light-activation of catalysts *via* sensitizer units provides a practical route for valorizing electrocatalyst design developments within the framework of solar-driven chemistry. We were curious to know if covalently attaching the well-known iron porphyrin electrocatalyst (Fe) with the typical ruthenium trisbipyridine sensitizer (Ru) would activate the system towards photocatalytic CO_2 reduction [1]. Photophysical studies of the Ru-Fe dyad, however, point to the complete extinction of the sensitizer unit that undergoes non-productive quenching process with the Fe catalyst - the unavoidable dilemma in this type of molecular assemblies. Nevertheless, in presence of exogenous Ru sensitizer, the Ru-Fe dyad presents a significant catalytic enhancement of the turnover number and CO_2-to-CO selectivity compared to the Fe catalyst analogue under the same conditions. Comprehensive analyses of the photophysical and electrochemical results suggest that the catalytic enhancement displayed by the dyad can be attributed to an interesting electron reservoir role played by the appended Ru moiety.

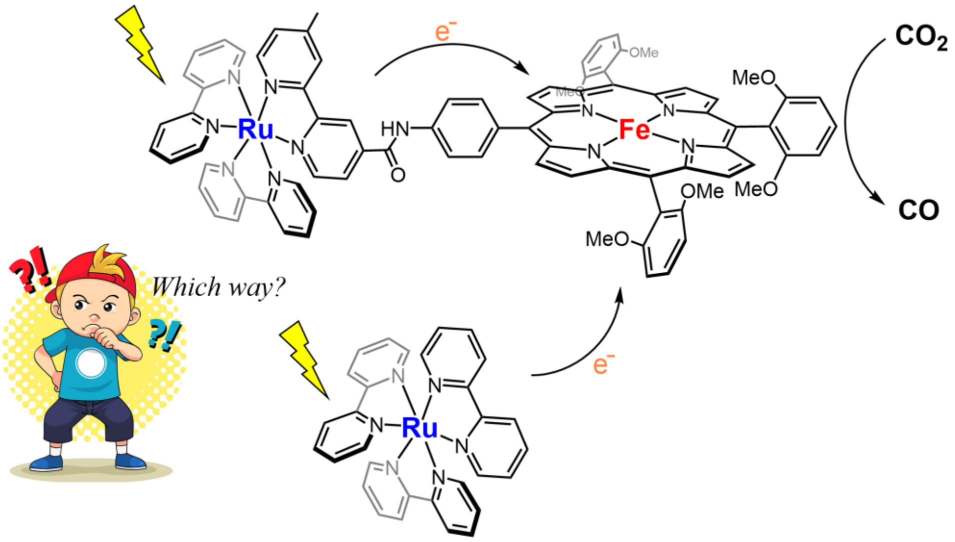

Figure 1. Molecular structure of Ru-Fe sensitizer-catalyst dyad.

[1] A. Trapali, P. Gotico, C. Herrero, M.-H. Ha-Thi, T. Pino, W. Leibl, G. Charalambidis, A. Coutsolelos, Z. Halime, A. Aukauloo, *Comptes Rendus. Chimie* **2021**, *24*, 1–14.

Thermopolymerization induced through the plasmonic excitation of gold nanoparticles

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Localized surface plasmon-induced polymerization of free-radical acrylate monomers is an efficient, smart, and versatile method for preparing metal/polymer hybrid nanoparticles (NPs) with accurate control of the thickness and spatial distribution of the polymer on the NP surface. Despite a growing number of practical demonstrations, the mechanism leading to polymerization of the acrylate monomer by localized surface plasmon resonance is still controversial. Indeed, trough decay processes, the plasmon emitted light, hot charge carriers and heat (Figure 1). If these processes are well-known, the main difficulty is to discriminate between them.

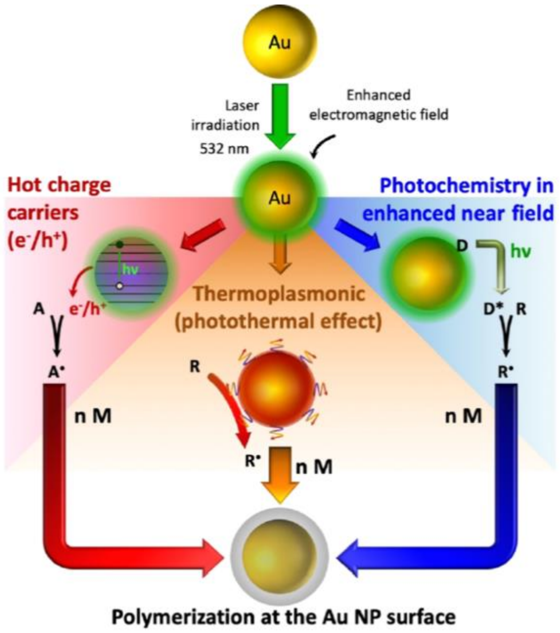

Figure 1. Schematic of the three main pathways to graft polymer through the plasmonic excitation of gold NPs. [1]

Previous experiments performed in the laboratory, highlighted the photochemical pathway as the main mechanism under mild irradiation. [1] The thermoplasmonic pathway was already used to cure InZnO thin films. [2] Here, we investigated thermoplasmonic to graft thermopolymer onto NPs. Different parameters are considered to address specifically thermopolymerization through the plasmonic excitation of NPs (i.e. single/assembly of NPs, continuous/pulsed laser excitation...).

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Broadband light-absorbing BODIPY-C60-distyryl BODIPY triad as heavy-atom-free organic triplet photosensitizers.

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Triplet photosensitizers have gained much attention due to their wide range of applications in photocatalysis, photodynamic therapy and triplet-triplet annihilation (TTA) upconversion.[1] To date, most of the triplet photosensitizer are based on heavy-atom effect while very few systems were reported for heavy-atom free organic triplet photosensitizers. In this work, we studied the triplet excited state properties of a novel broadband light-capturing multi-BODIPY-fullerene-based triad and its control dyads.[2] The two differently functionalized BODIPY units mounted on the two arms of a C_{60} core results in an extended UV visible absorption spectrum (300-700 nm), due to the cumulative absorptions of the two BODIPYs. Photoinduced processes leading to the formation of triplet states were elucidated in this family by steady-state and time-resolved emission, as well as transient absorption spectroscopy. Excitation of BODIPY chromophores can lead to the formation of a triplet state centered on C_{60} or the BODIPY moieties depending on the BODIPY structure. The use of these assemblies as potential organic triplet photosensitizers for triplet-triplet annihilation up-conversion was demonstrated. This work is useful for the development of a new wideband light-capturing, heavy-atom-free organic triplet photosensitizer, with an appreciably long triplet lifetime (280 µs) at room temperature.

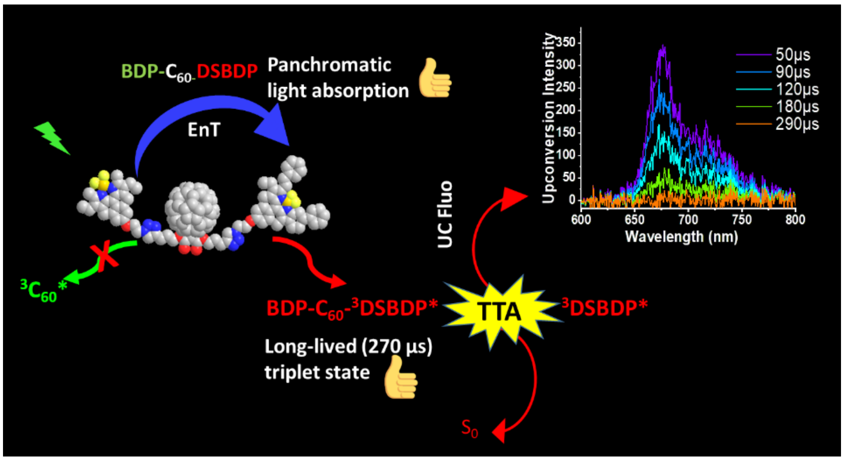

Figure 1. Formation of a long-lived triplet state on a broadband light-absorbing based on multi-BODIPY-fullerene triad.

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[2] A. Fatima, J. Rabah, E. Allard, H. Fensterbank, K. Wright, G. Burdzinski, G. Clavier, M. Sliwa, T. Pino, R. Méallet-Renault, K. Steenkeste, M.-H. Ha-Thi, *Photochem. Photobiol. Sci.* **2022**, *accepted.*

Universal Buffer: a powerful tool to investigate the impact of pH on photophysical and (photo)chemical properties from pH 1.9 to 12.

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pH can impact a wide range of (photo)chemical (kinetics, thermodynamics or quantum yield…) or photophysicals properties (absorption, emission…). We proposed to present an easy, fast and reproducible new method to tune with a very high precision pH value from 1.5 to 13 based on a so-called Universal Buffer. The latter is made of acetic acid, phosphoric acid and boric acid at 0.04 mol.L^{-1}. To ensure the efficiency and reliability of our procedure, we used it determine the pK_a value(s) for a series of indicators from sulfonephtalein derivatives [1] to azonaphtalen derivatives [2]. For BTB (BromoThymol Blue) impressive results were obtained (R^2 = 0,9999) and a pK_a of 7.13 ± 0.01 was found in perfect agreement with literature (7.1).

In addition, our procedure was applied to fluorescent compounds such as Quinine, Eosin Y, Rhodamine B and Riboflavine. For Quinine, absorption and emission properties (fluorescence quantum yield, absorption and emission spectrum) of the three acido-alkali forms (QH_2^{2+}, QH^+ and Q) were obtained (Figure 1) as well as pK_a and pK_a* and compare to the literature [3]. Potential applications in research can be also mentioned.

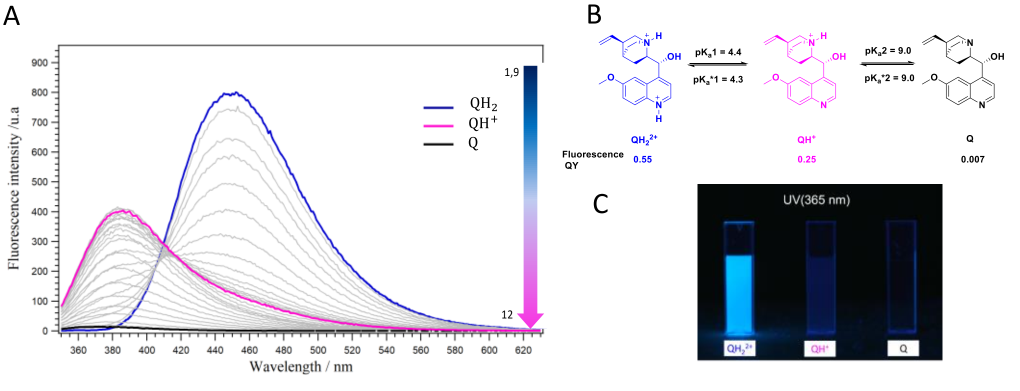

Figure 1. Series of fluorescence spectra from pH 1.9 to 12 for quinine. (B) Chemical structures, fluorescence quantum yield, pK_a and pK_a*and (C) image in the universal buffer under UV (365 nm) of the three acido-alkali forms of quinine

(1) BI, Ran; BRION, Aurélien; PERRIN, Rémi; DORÉ, Clément; CLAVIER, Gilles; Piard, J.; L.Shi. Utilisation d'un Tampon Universel pour l'étude d'indicateurs colorés Acido-Basiques (Par Spectrophotométrie UV-Visible). *Bulletin de l'Union des Physiciens* **2019**, *1014*, 559–601.
(2) BI, Ran; BRION, Aurélien; PERRIN, Rémi; DORÉ, Clément; Piard, J.; L.Shi. Utilisation d'un Tampon Universel Pour l'étude d'indicateurs Colorés Acido-Basiques (Par Spectrophotométrie UV-Visible). *Bulletin de l'Union des Physiciens* **2019**, *1015*, 661-.
(3) Article Accepted. *Bulletin de l'Union des Physiciens*.

Conformation isomerism of 1–indanol probe by PhotoElectron Circular Dichroism

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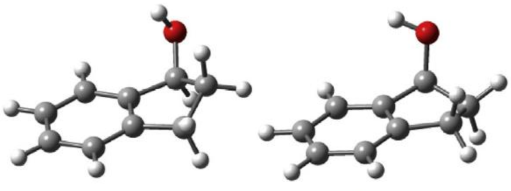
PhotoElectron Circular Dichroism (PECD) allows measuring the forward/backward asymmetry of the angular distribution of photoelectrons with respect to the axis of light propagation following the ionization of a chiral molecule by circularly polarized light.[1] This technique is very sensitive to the molecule conformations. That is why we applied it to a flexible chiral molecule derived from indane. 1-indanol shows two quasi-isoenergetic conformers connected by a ring inversion motion whose relative population depends on the carrier gas.[2]



1_{eq} 2_{ax}

Figure 1. Conformers of 1-indanol present in a supersonic jet in argon (1_{eq}) and in helium (1_{eq} et 2_{ax}).

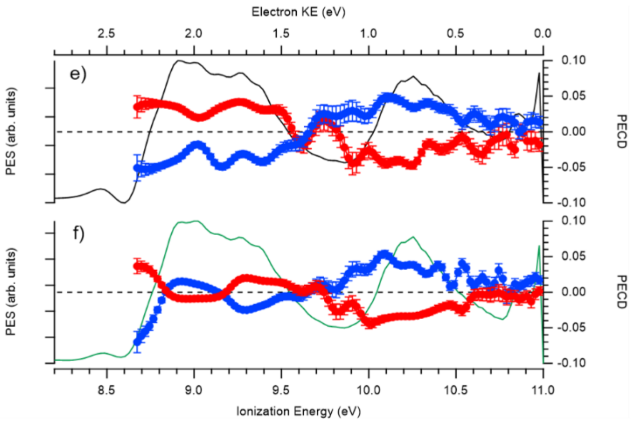


Figure 2. Photoelectron spectra in argon (black) and in helium (green). PECD spectra of R-indanol (blue) and of S-indanol (red) recorded at hν=11eV

The photoelectron (PES) and PECD spectra of S-indanol and R-indanol under supersonic conditions were recorded for both gases at several photon energies on the DESIRS beamline at the synchroton SOLEIL. In helium, two conformers were probed at the same time while in argon only one conformer was probed. First, the PECD spectra show a very nice expected mirroring effect between the two enantiomers in the same gas. On the other hand, clear differences between the two gases due to the contributions of two or one conformers are observed. The experimental results were supplemented by quantum calculations to better understand the nature of the orbitals ionized in these conditions.

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Investigation of the optical properties of single nanographene

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Graphene is a key material for nanoelectronics. Nevertheless, its zero gap makes it unsuitable for applications needing semiconductors with sizeable energy gaps. One way to open a gap in graphene is to use size reduction effects. The reduction of one dimension leads to carbon nanotubes and graphene nanoribbons that are 1D carbon nanostructures. Reducing one more dimension leads to 0D graphene quantum dots. The optical properties of carbon nanotubes have been investigated for approximately 20 years, while the study of graphene quantum dots and nanoribbons is at its infancy. Among potential application of these sp2 carbon nanostructures, the use of graphene nanoribbons and quantum dots as light emitters attracts a lot of attention. Here, I will present our recent results on the investigation optical properties of single nanographenes synthesized by bottom-up chemistry [1-4].

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[4] C. Elias et al, in preparation

RESUMES

Posters

Synthèse de nouvelles molécules pour la photoéjection de cation à l'état excité

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Les interrupteurs moléculaires basés sur des processus photochimiques reposent principalement sur des réactions de photoisomérisation, de photocyclisation ou de phototransfert de proton (photoinduced proton transfer PPT).[1] Pourtant, peu de papiers ont exploré des réactions analogues au PPT en remplaçant le proton par un autre ion. Ainsi, peut-on envisager un transfert d'ion à l'état excité équivalent à la réaction d'un photoacide. En 2002, Plaza *et al* ont montré qu'un composé à base de DCM conduisait à la photoéjection de Sr^{2+}.[2] En 2004, Moore *et al* ont montré qu'un complexe de rhénium photoéjecte à l'état excité un ion Ca^{2+} (**Figure 1a**).[3] Récemment, Aloïse *et al* ont mis en évidence la possibilité de photoéjection avec des molécules organiques de type bétaïne pyridium.[4] Notre but est de synthétiser de nouvelles molécules organiques et organométalliques pour établir une base de données de molécules capables de photoéjecter des cations. La synthèse des molécules et les études spectroscopiques s'appuient conjointement sur des calculs DFT et TD-DFT. Perrier *et al* ont montré, pour le complexe synthétisé par Moore en 2004, qu'il est possible de prédire la photoéjection par des méthodes quantiques.[5] Nous proposons de présenter la synthèse ainsi que la spectroscopie stationnaire et la spectroscopie résolue en temps (femtoseconde et nanoseconde) d'un complexe bisterpyridine iridium $[Ir(tpy)(tpyaza)](PF_6)_3$ (**Figure 1b**).

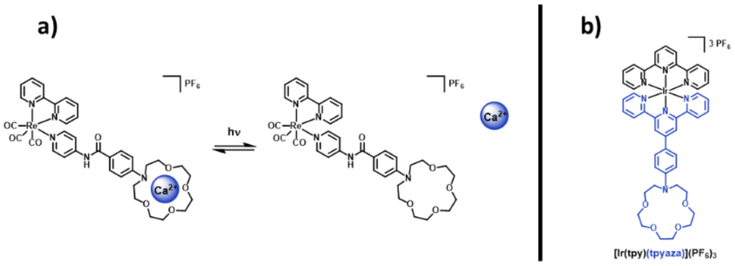

Figure 1. a) Réaction de photoéjection de calcium pour le complexe synthétisé par Moore *et al*. **b)** Structure du complexe d'iridium étudié et présenté.

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4,4’-Dimethylazobenzene: A New Chemical Actinometer

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Chemical actinometers are an essential tool to measure the photon flux of a light source and carry out quantitative analysis on photoreactions. [1] However, most of the actinometers employed so far show minor drawbacks, such as difficult data treatment, parasite reactions, low stability or impossibility to reset and reuse. We propose herewith the use of 4,4’-dimethylazobenzene as a new performant and handy chemical actinometer. [2] This azobenzene derivative undergoes a highly efficient E/Z isomerization, approaching total conversion upon irradiation at 365 nm. We carefully determined the photoisomerization quantum yields and set up a facile actinometric protocol that requires the sole use of a spectrophotometer to determine the photon flux. Moreover, after full conversion to the Z form, the Z-E photoisomerization can be exploited for actinometry in the visible region. Finally, thanks to the excellent fatigue resistance, after thermal or photo-isomerization (e.g. at 254 nm) the same solution can be reused several times.

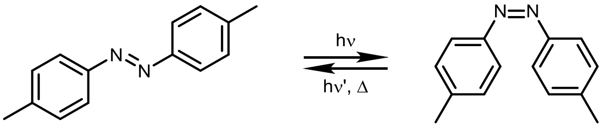

Figure 1. Structure and photoisomerization of 4,4’-dimethylazobenzene.

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Synthesis and studies of dipyrido[1,2-b:1',2'-e][1,2,4,5]tetrazine and derivatives : towards the organic electronics applications.

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π-Conjugated molecules have attracted much attention as materials for the development of organic electronics. Numerous structures have already been published[1] but the search for new architectures is still very active.

Polycyclic aromatic 1,4-dihydro-s-tetrazines, have a strong potential for such applications as electron donors because they are easily oxidized. In addition, they absorb light between 300 nm and 700 nm depending on their structure. However, these compounds have never been used in organic electronic.

The synthetic route to obtain such molecules is described in Figure 1[2,3]. The use of a so-called "electrophilic nitrogen" reagent is necessary in order to create a nitrogen-nitrogen single bond. A cyclization step follows to form the tetrazine ring.

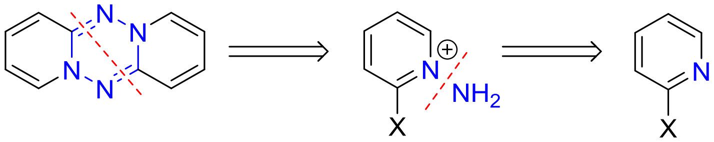

Figure 1 : Retro-synthesis of dipyrido[1,2-b:1',2'-e][1,2,4,5]tetrazine

Using this method several tetrazines have been prepared and in particular di-halogenated tetrazines (Figure 2).

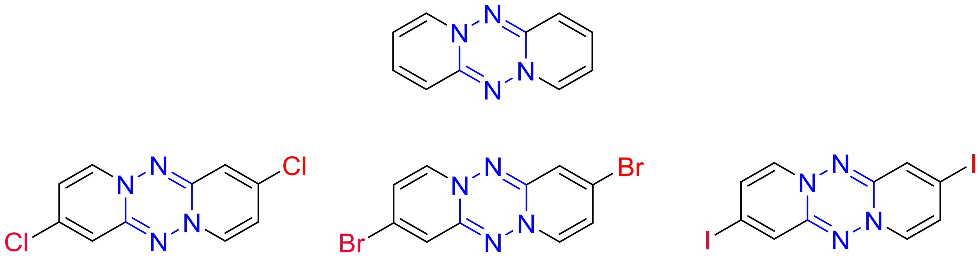

Figure 2 : dipyrido[1,2-b:1',2'-e][1,2,4,5]tetrazine and its di-halogenated derivatives.

The photophysical properties of the series have been studied in solution and rationalized with DFT calculations. These compounds represent a first step toward functional molecular materials since the halogen atoms will then be used to perform organometallic couplings

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Competitive photoisomerization and energy transfer processes in fluorescent multichromophoric systems

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Multichromophoric systems showing both fluorescence and photoisomerization are fascinating, with complex interchromophoric interactions. The experimental and theoretical studies of a series of compounds, bearing two and three 4-dicyanomethylene-2-*tert*-butyl-6-(*p*-(*N*-(2-azidoethyl)-*N*-methyl) aminostyryl)-4H-pyran (DCM) units are reported. The photochemical properties of multi-DCM derivatives, namely **2DCM** and **3DCM**, were compared to the single model azido-functionalized **DCM**, which exists in two forms (*E* and *Z* isomers, **Figure 1a**). Steady-state spectroscopy and photokinetics experiments under UV or visible irradiation indicated that intramolecular energy transfer processes take place among the DCM units. Homo- as well as hetero-energy transfer processes between adjacent chromophores were further confirmed by anisotropy and time-resolved fluorescence experiments (**Figure 1b, 1c**). Molecular dynamics (MD) simulations for **2DCM** were carried out and analyzed using a Markov state model, providing geometrical parameters (mutual orientation and distance between chromophores) and energy transfer efficiency. This work contributes to a better understanding and rationalization of multiple energy transfer processes occurring within multichromophoric systems.

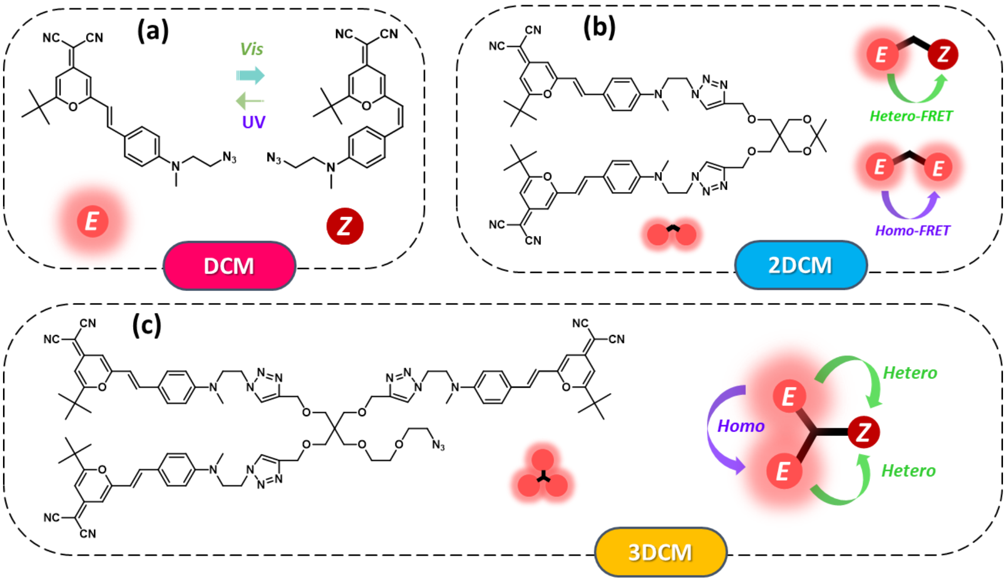

Figure 1. (a) *E*↔*Z* photoisomerization illustration of the model azido DCM molecule. **(b)** Structure of (*EE*)-**2DCM** and intramolecular energy transfer processes (homo-FRET and homo-FRET) illustration. **(c)** Structure of (*EEE*)-**3DCM** and intramolecular energy transfer processes illustration.

Photocatalytic biodiesel production from feedstocks with high fatty acid content

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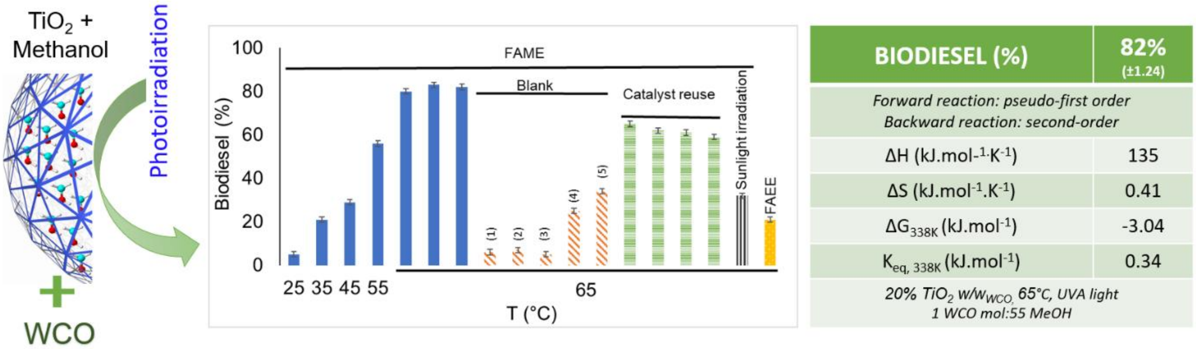
Biodiesel was produced by TiO_2-photocatalysis via simultaneous esterification and transesterification. Using a feedstock with high content of free fatty acid (89% triglycerides and 11% free fatty acid) and methanol high conversions of 89% ±1.24 were obtained under optimized conditions (1mol feedstock:55mols MeOH, 20% TiO_2 $w/w_{feedstock}$, 65°C, batch reactor, 4 hours, UVA light). The recovered photocatalyst was reused and a conversion of 59% was achieved after 5 cycles. The kinetic data was adapted to a mathematical model which considered pseudo-first forward and second-order backward reactions. The predicted data showed high accuracy (R^2 of 0.996, Matlab®). The thermodynamic properties indicate that the endothermic reaction is irreversible, but feasible only at temperatures higher than 65°C. This study demonstrates that heterogeneous photocatalysis can be efficiently applied to biodiesel production [1]. The developed procedure overcomes some of the challenges frequently found in the traditional thermal process using strong acids and bases. It avoids elevated temperatures, extreme pH ranges, unfavourable catalyst conditions (removal, reuse) or low product purity, respectively.



BIODIESEL (%)	82% (±1.24)
Forward reaction: pseudo-first order *Backward reaction: second-order*	
ΔH ($kJ.mol^{-1.}K^{-1}$)	135
ΔS ($kJ.mol^{-1}.K^{-1}$)	0.41
ΔG_{338K} ($kJ.mol^{-1}$)	-3.04
$K_{eq,\ 338K}$ ($kJ.mol^{-1}$)	0.34
20% TiO_2 $w/w_{WCO,}$ 65°C, UVA light *1 WCO mol:55 MeOH*	

Figure 1. Biodiesel production of waste cooking oil (WCO) using TiO_2-photocatalysis [FAME: fatty acid methyl ester; FAEE: fatty acid ethyl ester; Blanks: (1) absence of TiO_2, (2) absence of irradiation, (3) absence of TiO_2 and irradiation, (4) absence of stirring and (5) absence of TiO_2 pretreatment].

[1] R. A. Welter, H. Santana, L. G. de la Torre, M. Robertson, O. Pereira Taranto, M. Oelgemöller, *ChemPhotoChem*, **2022**, *Volume*, in print (DOI: 10.1002/cptc.202200007).

Development of Mechanofluorochromic Surfaces as Force Sensors

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Mechanofluorochromic compounds have the capacity to change the color of their emission if they are subject to a mechanical stress. Therefore, they can be used to determine mechanical stress such as pressure or shearing. Among them, polydiacetylenes are a very interesting class as they can switch between a blue non-emissive form and a red emissive one. The blue form is obtained by photopolymerization of diacetylene and turns red after an application of either a mechanical activity or a thermal change. The reversibility of the transition, as well as the fluorescent change between the blue and the red form in a short time, opens the path to the creation of captors based on those molecules. We present herewith the covalent grafting of polydiacetylenes onto glass surfaces and their characterization via spectroscopy, microscopy or wettability measurements. These preliminary results pave the way to the coating of different substrates (e.g. microfluidics chips) and finally achieve fluorescent sensors for microscale forces.

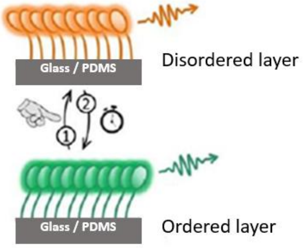

Figure 1. Emission change of mechanofluorochromic molecules covalently grafted on glass or PDMS.

[1] Adv. Mat., 2016, 28, 6, 1073-1095

[2] Chem. Mater. 2019, 31, 4, 1196-1222

[3] Chem. Commun., 2019, 55, 14566-14569

QUANTUM DOTS CdSe-ZnS WITH AN AROMATIC DITHIOCARBAMATE LIGAND AS POSSIBLE MERCURY SENSOR

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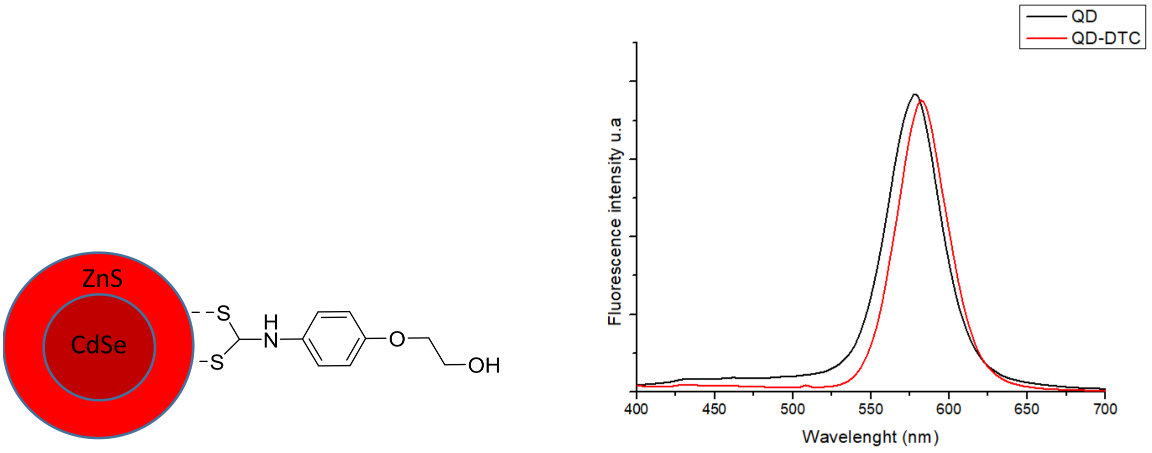
In recent years, the development of quantum dots (QDs) for use in detecting metal ions and biological species has attracted increasing attention because of their excellent optoelectronic properties. Mercury ion pollution results from the illegal gold mining mainly in countries such as Indonesia and Colombia, which is harmful for public health and the environment. Analysis of mercury requires specialized tools and is not possible on-site. To address this problem the current work concerns quantum dots modified with an aromatic dithiocarbamate (DTC) ligand as mercury sensor. The DTC ligand was capped in QDs with exchange ligand using hexane (QDs) and methanol (DTC) at 60°C for 1 hour, following the changes in UV-Vis and fluorescence spectrum. The absorption and fluorescence spectra of DTC capped QDs display a red shift with respect to the initial QDs, the emission maximum change from 578 to 582 nm due to the delocalization of the exciton over the ligand shell [1]. In addition, the exchange ligand shows a small quenching of fluorescence, due the electron donor influence of hydroxyl group in the DTC [2]. Finally, the QDs was solubilized in ethanol to evaluate the detection of mercury using concentrations from 0.5-5μM, the fluorescence of new QDs show a quenching with the increasing of mercury concentration.



a) **b)**

Figure 1. a) Representation QD-DTC, **b)** Exchange Ligand Fluorescence Spectrum

[1] Matthew T. Frederick, Victor A. Amin, Laura C. Cass, and Emily A. Weiss, Nano Letters, **2011**, 11, 5455-5460.

[2] Meghan B. Teunis, Sukanta Dolai, and Rajesh Sardar, Langmuir, **2014**, 30, 7851-7858.

Photophysical properties of negative photochromic compounds in solution

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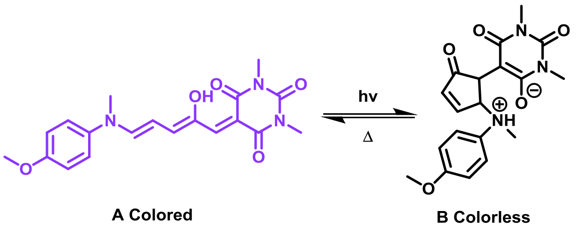
Positive photochromic molecules are known and studied for decades[1] , [2]. However, in the last few years, new families of photochromic molecules were discovered, for which the stable form A is colored and, thanks to irradiation with visible light, can be transformed into the colorless isomer B: this class of molecules is called "negative" photochromic compounds [3]. In this work, the properties of negative photochromic derivatives, belonging to the Donor-Acceptor Stenhouse Adducts (DASA) family, will be presented in solution (Figure 1, left) [4]. Steady-state spectroscopy was carried out in solution to provide the main spectral characteristics, whereas the continuous acquisition of absorption spectra in the presence or absence of illumination allows highlighting three major phenomena for the DASA compounds when dissolved in solution (Figure 1, right): a "dark equilibrium" which has been also followed by NMR, a "photostationary state" under irradiation, and a "thermal back reaction" in absence of light. Photophysical properties such as the conversion ratio, the quantum yield, and the kinetic rates can be extracted from photokinetics and the correlation between UV-vis absorption spectroscopy and NMR.



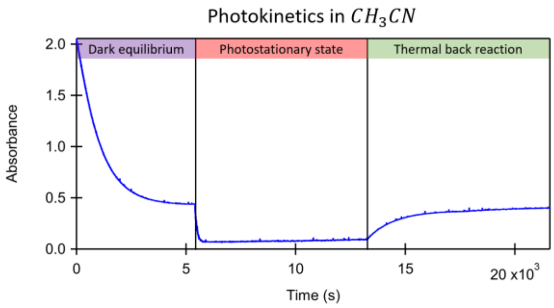


Figure 1 : (Left) Photochromic reaction of the DASA compound investigated in this work [4]. (Right) Photokinetic experiment showing the three distinct phenomena of a DASA in solution in the absence or presence of light (absorbance is measured at 580 nm, in the absorption band of the colored form, irradiation is carried out at 575 nm).

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[1] *K. Nakatani, J. Piard, P. Yu, R. Métivier, Introduction: organic photochromic molecules, in Photochromic materials: preparation, properties and applications, 1st ed. (Eds.: H. Tian, J. Zhang), Wiley-VCH,* ***2016****, pp. 1-45.*

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[3] *M. M. Lerch, W. Szymanski, B. L. Feringa, The (photo)chemistry of Stenhouse photoswitches: guiding principles and system design, Chem. Soc. Rev.* ***2018****, 47, 1910-1937.*

[4] *N. Mallo, E. D. Foley, H. Iranmanesh, A. D. W. Kennedy, E. T. Luis, J. Ho, J. B. Harper, J. E. Beves, Structure-function relationships of donor-acceptor Stenhouse adduct photochromic switches, Chem. Sci.* ***2018****, 9, 8242-8252.*

Excited-states of 1,10-phenanthroline derivatives and related Ru(II) (nano-)edifices for potential applications

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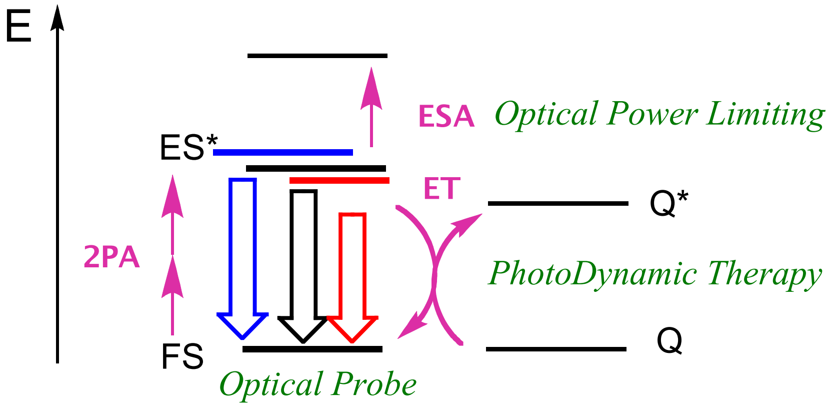
The presentation will concern studies in the field of the linear and nonlinear optical properties of ligands and related Ru(II) complexes [1]. One- and two-photon induced (2PI) access to ^{3}MLCT excited states will be discussed both in a fundamental interest and in the perspective of potential applications in physics and biology such as photodynamic therapy (PDT) [2]. The access to functionalized surfaces [3] and nano-particles [4] will also be presented and discussed in the perspective of applications in theranostic [5].



1) E. Rousset, O. Mongin, J. Moreau, L. M. Lawson Daku, M. Beley, P. C. Gros, S. Chevreux, M. Blanchard-Desce, G. Lemercier, *Dalton Trans.*, **2021**, ***50***, 10119.
2) G. Lemercier, M. Four, S. Chevreux, *Coord. Chem. Rev.*, **2018**, *368*, 1.
3) Van Q. Nguyen, X. Sun, F. Lafolet, J.-F. Audibert, F. Miomandre, G. Lemercier, F. Loiseau, J.-C. Lacroix, *J. Am. Chem. Soc.*, **2016**, *138*, 9381.
4) Q. Nguyen, E. Rousset, V. Nguyen, V. Colliere, P. Lecante, W. Klysubun, K. Philippot, J. Esvan, M. Respaud, G. Lemercier, P. Tran, C. Amiens, *ACS Applied Materials & Interfaces*, **2021**, ***13*,** 45, 53829.
5) C. Truillet, F. Lux, J. Moreau, M. Four, L. Sancey, S. Chevreux, G. Boeuf, P. Perriat, C. Frochot, R. Antoine, P. Dugourd, C. Portefaix, C. Hoeffel, M. Barberi-Heyob, C. Terryn, L. van Gulick, G. Lemercier, O. Tillement, *Dalton Trans.*, **2013**, *42*, 12410; S. Lechevallier, R. Mauricot, H. Gros-Dagnac, S. Chevreux, G. Lemercier, E. Phonesouk, M. Golzio, M. Verelst, *ChemPlusChem.*, **2017**, *82*, 770

Ultrafast Excited State Dynamics of the Archae-Rhodopsin 3 and its mutants

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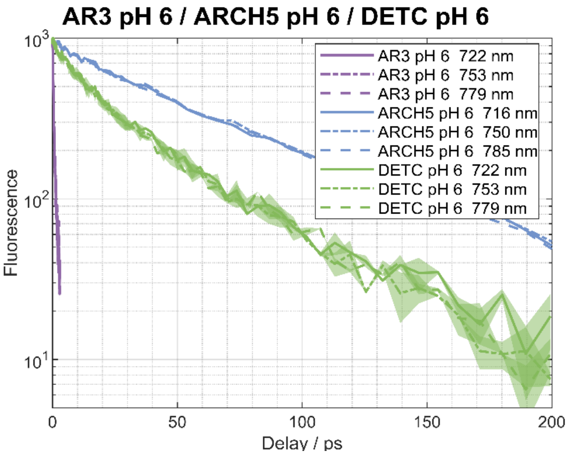

Figure 1: *Fluorescence decays of AR-3, and the two mutants DETC and Arch-5, at pH6 on a semi-log scale*

Archaerhodopsin-3 (AR-3), is a VIS light-sensitive retinal protein found in *Halorubrum sodomense*, where is contributes to a primitive form of photosynthesis (transmembrane proton pumping). As most microbial rhodopsins, AR-3 displays a sub-picosecond trans/cis photo-isomerization of the retinal chromophore, hence these proteins are non-fluorescent. However, in the early 2010, AR-3 has attracted attention for applications in optogenetics [1]. It was shown that the voltage-sensitive fluorescence is due to sequential 3-photon excitation needed to induce fluorescence from the photo-cycle intermediate Q [2]. However, multiple mutants then emerged [3], with fluorescence quantum yields (FQY) reaching up to 1.2%, upon 1-photon absorption, which is a 100-fold increase with respect to the wild-type protein (wt). In order to understand this exceptionally strong effect of the mutations in detail, we studied the fluorescence decay kinetics for wt as a function of pH ≤ 6, since protonation of the counter ion is known to prolong the excited state lifetime of rhodopsins. Other changes in terms of the electrostatic interactions of the protein cavity with retinal are induced in the double mutant DETC and in the quintuple mutant Arch-5 [3]. The fluorescence kinetics (figure 1) are measured with 200 fs time resolution using a broadband up-conversion set-up. We find them to be best described by a sum of 3 decaying exponentials, which represent the heterogeneity of protein environment. The average excited state lifetimes reach high values up to 65 ps (figure 1). For DETC and Arch-5, the results are in agreement with the reported FQY's [3].

A detailed comparison with QM/MM simulations (V. Ledentu, N. Ferré & M. Olivucci) is in progress.

[1] Kralj, J. M., et al., *Nat. Methods* **2011,** *9*, 90–95.

[2] Maclaurin, D., et al.,*Proc. Natl. Acad. Sci.* **2013**, *110*, 5939–5944.

[3] McIsaac, R.S, et al.,*Proc. Natl. Acad. Sci.* **2014**, *111*, 13034-13039.

Combination of two amplification phenomena for high-sensitivity detection

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Terarylenes are a specific family of photochromic diarylethenes where certain derivatives can undergo the cascading effect (CE): a single oxidation input may cause the spontaneous ring opening of up to 1000 terarylene units.[1] On the other hand, amplified fluorescence photo-switching (AFPS) has been observed in nano-size materials, where switching a single photochromic unit can cause large scale energy transfer (here namely FRET - Förster Resonance Energy Transfer) and therefore fluorescence quenching of up to 400 fluorophores.[2] Combining these two phenomena can lead to highly sensitive detectors, where an external trigger can cause a change in the absorption properties of the terarylene which in turn is detected via fluorescence quenching.

As the first steps for this purpose, BODIPY and terarylene derivatives were synthesized. Also, as a model system for describing FRET, the BODIPY derivative was paired with a commercially-available photochromic compound in a polymer matrix. FRET efficiency, fatigue resistance, and fluorescence and absorption profiles were investigated as a function of irradiation time.

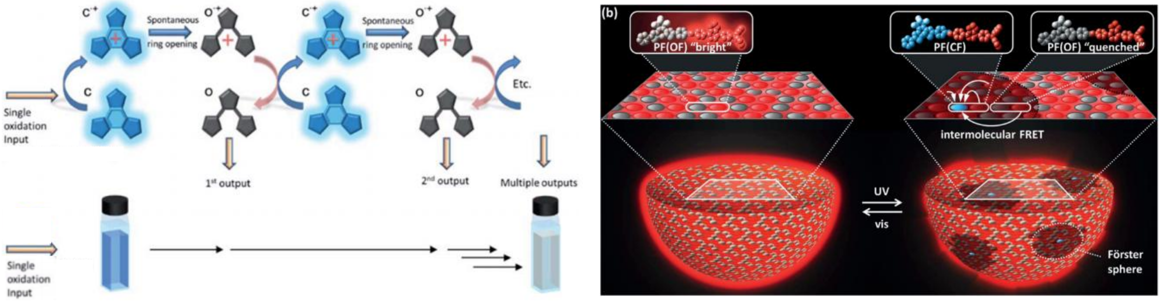

Figure 1. Illustration of the two amplification phenomena: Cascading Effect (CE, **left**) and Amplified Fluorescence Photo-Switching (AFPS, **right**).

[1] Asato, R., Martin, C. J., Calupitan, J. P., Mizutsu, R., Nakashima, T., Okada, G., Kawaguchi, N., Yanagida, T., Kawai, T., *Chem. Sci.*, 2020, 9 (11), 2504-2510.

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Fluorescence photoswitching of diarylethene dyads: characterization of the energy transfer and microscopy

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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, fluorescence photoswitching was performed on individual nanoparticles, allowing us to observe an interesting fluorescence recovery profile. To explain such an uncommon behavior, a mathematical modeling was proposed, allowing the determination of the number of perylenediimides quenched per photochromic molecule. Preliminary experiments of super-resolution imaging will be presented.

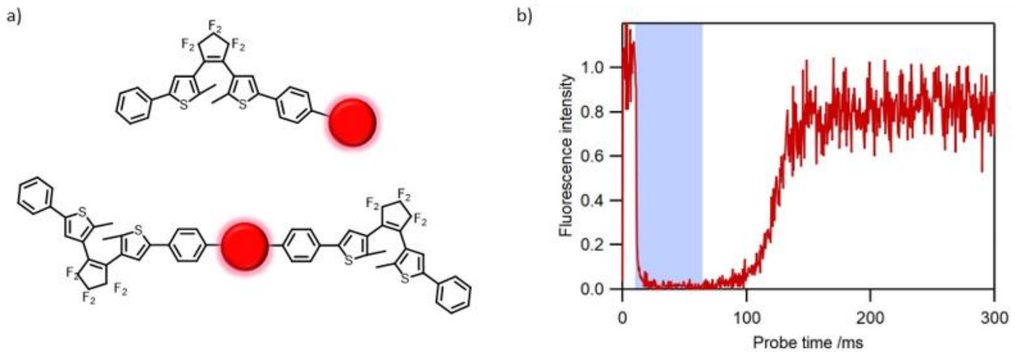

Figure 1. a) Schemes of diarylethene derivatives linked to fluorophores (red circles), b) fluorescence photoswitching profile of a single nanoparticle (the blue area corresponds to UV irradiation).

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

[2] I. Ikariko, S. Deguchi, N. Fabre, S. Ishida, S. Kim, S. Kurihara, R. Métivier, T. Fukaminato, *Dyes and Pigments* **2020**, 180, 108490

Activation photocontrôlée de la *N,N'*-bis[3,5-bis(trifluorométhyl)phényl]thiourée portant des groupements protecteurs photolabiles dérivés de coumarine

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Le contrôle spatio-temporel des processus catalytiques a séduit les chercheurs depuis plusieurs décennies. Dans ce contexte, l'incorporation d'un groupement protecteur photolabile dans la structure d'un catalyseur fonctionnel est une stratégie couramment utilisée pour l'initiation d'une transformation chimique par irradiation à une longueur d'onde donnée.[1]

La *N,N'*-bis[3,5-bis(trifluorométhyl)phényl]thiourée (thiourée de Schreiner) est un organocatalyseur capable d'activer par liaison hydrogène une grande variété de substrats, donnant lieu à des applications couvrant une large gamme de transformations organiques.[2] Nous décrirons ici nos résultats récents concernant la désactivation de ce catalyseur à l'aide de groupements protecteurs dérivés de la coumarine, ainsi que sa libération contrôlée par la lumière dans le but de photo-initier des transformations catalytiques (Figure 1).

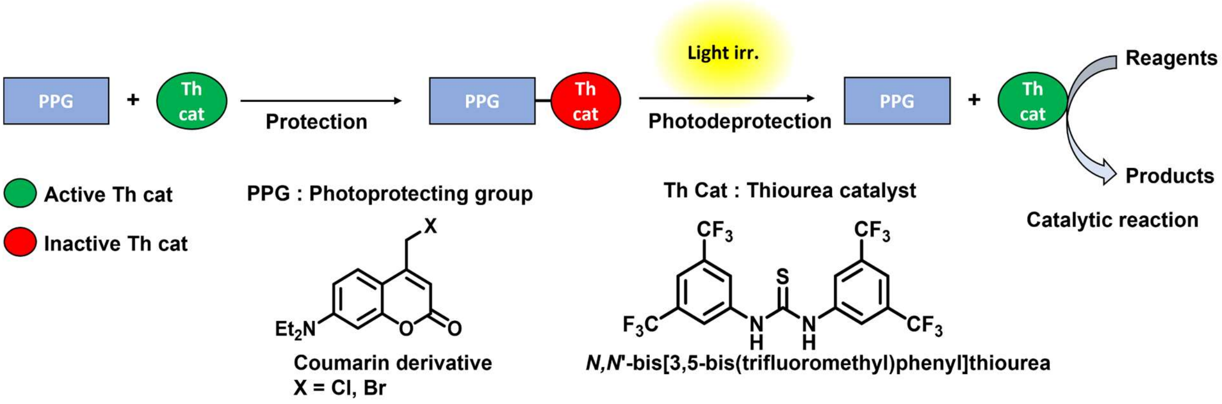

Figure 1. Synthèse d'une thiourée de Schreiner photocagée et sa photodéprotection pour le contrôle de transformations catalytiques.

[1] (a) R. S. Stoll, S. Hecht, *Angew. Chem. Int. Ed.* **2010**, *49*, 5054–5075. (b) C. Brieke, F. Rohrbach, A. Gottschalk, G. Mayer, A. Heckel, *Angew. Chem. Int. Ed.* **2012**, *51*, 2–33. (c) C. Deo, N. Bogliotti, P. Retailleau, J. Xie, *Organometallics* **2016**, *35*, 2694–2700. (d) R. Weinstain, T. Slanina, D. Kand, P. Klán, *Chem. Rev.* **2020**, *120*, 13135–13272.

[2] (a) Z. Zhang, P. R. Schreiner, *Chem. Soc. Rev.* **2009**, *38*, 1187–1198. (b) Z. Zhang, Z. Bao, H. Xing, *Org. Biomol. Chem.* **2014**, *12*, 3151–3162.

Molecular dye-based Fluorescent Organic Nanoparticles: a bright 10 years story

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For the last decade, our group has been developing a new class of ultra-bright fluorescent nanoparticles *via* a bottom-up approach based on the design of dedicated organic Polar and Polarizable Dyes (PPDs) that spontaneously form fluorescent organic nanoparticles (FONs) upon self-aggregation in water. Via subtle molecular engineering of the PPD, we could achieve fluorescent nanoparticles combining small size (Ø 10-50 nm), very large one and two-photon brightness (up to (up to 10^8 $M^{-1}cm^{-1}$ and 10^6 GM), remarkable structural and colloidal stability, tunable emission (from blue to NIR1), good photostability as well as biocompatibility (*in cellulo* and *in vivo*). As such, these non-covalent fully organic nanoparticles represent an easy to prepare, versatile and highly promising alternative to quantum dots for bioimaging purposes.[1-3] Furthermore, their surface properties can be engineered to yield tunable, hyper-bright and photostable NPs that either easily penetrate inside cells while maintaining their integrity (allowing single particle tracking within cells)[2] or alternatively can be made naturally stealthy and diffuse deep into the brain's extracellular space.[3] Future developments include surface functionalization for biosensing and cellular targeting. *In this poster, we will present the history of the FONs developed in the team from the 2010's until now.*

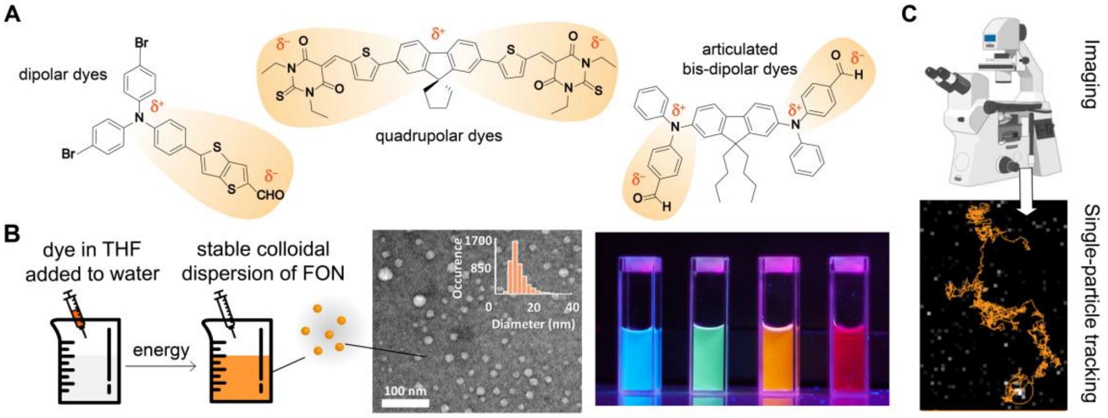

Figure 1. From molecular design of PPDs (A) to FONs (B) and application to bioimaging (C)

[1] a) V. Parthasarathy et al, Small, 7 (2011), 3219. b) K. Amro et al, Tetrahedron, 70 (2014), 1903. c) C. Mastrodonato et al, Molecules, 21 (2016), 1227. d) Verlhac J.-B., Daniel J., Pagano P., Clermont G., Blanchard-Desce M., C. R. Chimie, 19 (2016), 28.

[2] a) E. Genin et al, Adv. Mater., 26 (2014), 2258. b)J. Daniel et al, J. Phys. D: Appl. Phys., 49 (2016), 084002.

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