



French, Swiss and German Conference on Photochemistry, Photophysics and Photosciences

CP2P'23

15, 16, 17 May 2023

Mulhouse, France



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Welcome !

L'Université de Haute-Alsace in Mulhouse is very pleased to welcome you to the French, Swiss and German Conference on Photochemistry, Photophysics and Photosciences CP2P'23.

These scientific days are organized under the impetus of the Subdivision Photochemistry, Photophysics and Photosciences (SP2P) of the Division of Physical Chemistry (Société Chimique de France & Société Française de Physique), along with the support of the Swiss Chemical Society (SCS), the GDCh-Fachgruppe Photochemie and the European Photochemistry Association (EPA).

The location of Mulhouse, at the crossing of the 3 frontiers, offers an opportunity to give an international dimension to these annual scientific days. The objective is to gather the community of photochemists and photophysicists, with the possibility for students and young researchers to present their work, in a relaxed, constructive and friendly atmosphere. It is also the chance to listen to confirmed renowned researchers, either experimenters or theoreticians. For this edition, we have indeed the honor to welcome several invited speakers:

- Prof. J.V. Milić, University of Fribourg (CH)
- Prof. S. Hecht, Humboldt University Berlin (DE)
- Dr. M. Chavarot-Kerlidou, Lab. de Chimie et Biologie des Métaux, CEA Grenoble (FR)
- Prof. M. Oppermann, University of Basel (CH)
- Dr. C. Gazon, University of Bordeaux, ISM (FR)
- Prof. C. Kerzig, Johannes Gutenberg University Mainz (DE)
- Prof. D. Wöll, RWTH Aachen University (DE)
- Dr. C. Bizzarri, Karlsruhe Institute of Technology (DE)
- Dr. L. Favereau, Université de Rennes 1 (FR)

We wish you a warm welcome and we hope you will fully enjoy these days!

The organizing committee



Keynote speakers



Prof. J.V. Milić

University of Fribourg (CH)

*Enhanced Functionality of
Hybrid Materials in Photovoltaics*



Prof. S. Hecht

Humboldt University Berlin (DE)

*Illuminating Materials, Devices,
and Manufacturing with Photoswitches*



Dr. M. Chavarot-Kerlidou

Lab. de Chimie et Biologie des Métaux, CEA Grenoble (FR)

*Fundamental challenges in the design of performant
dye-sensitized photocathodes for solar fuels production*



Invited speakers



Prof. M. Oppermann

University of Basel (CH)

*Molecules in motion: Capturing and controlling
molecular dynamics through chirality*



Dr. C. Grazon

University of Bordeaux, ISM (FR)

*From Quantum Dots to Fluorescent Organic Nanoparticles:
bright nanotools for biosensing*



Prof. C. Kerzig

Johannes Gutenberg University Mainz (DE)

One UV photon or two blue photons, that is the question



Prof. D. Wöll

RWTH Aachen University (DE)

*Super-resolution fluorescence imaging of microgels
New insights into their structure and properties*



Dr. C. Bizzarri

Karlsruhe Institute of Technology (DE)

Molecular photo-driven CO₂ reduction by earth-abundant systems



Dr. L. Favereau

Université de Rennes 1 (FR)

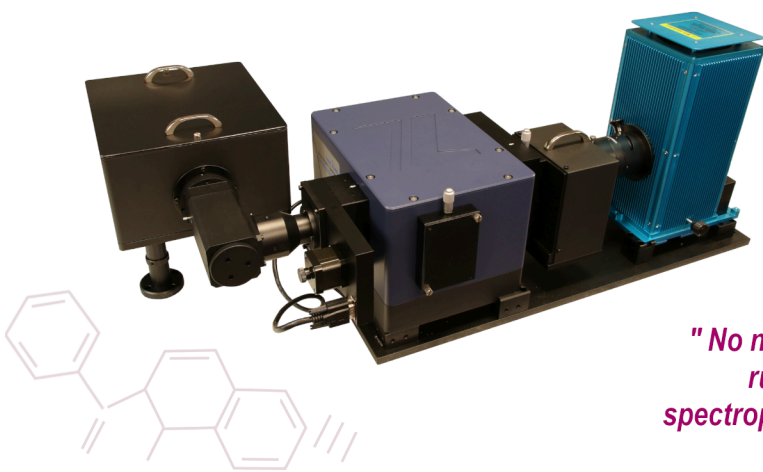
*Chirality in molecular materials and
related photophysical properties*



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Photo-crystallography



Venue



The conference will take place in the building of the Faculté des Sciences et Techniques du campus de l'illberg de l'Université de Haute-Alsace.
The conference room is the Amphithéâtre Gaston Berger (GB)

Address:

Faculté des Sciences et Techniques (building K on the map)
18 Rue des Frères Lumière,
68200 Mulhouse

<https://www.uha.fr/resource/plan-dacces/plan-campus-illberg.pdf>





How to come ?



By train:

Regular connections Paris-Mulhouse (3h) and Strasbourg-Mulhouse (1h) then bus or tramway from Mulhouse station.

<https://www.sncf-connect.com/>

Access from SNCF Mulhouse station:

Tramway - ligne 2 - arrêts "Illberg"

All details on :

<http://www.solea.info/se-deplacer/horaires-des-lignes/votre-itineraire>

By car:

Mulhouse is located at the junction of the A36 (5 hours from Paris) and A35 freeways.

From the freeway, take the exit "Les Coteaux" towards the RD 68 (expressway) - exit n°3 (Mulhouse Centre, Brunstatt).

By plane:

Airport : Euroairport Basel-Mulhouse (30km from Mulhouse) then train to Mulhouse Station then bus or Tramway from Mulhouse Station.

Companies : Air France, Easyjet (Bordeaux, Toulouse, Montpellier, Nice, ...), KLM, Lufthansa,

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Organizing committees

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We warmly thank our institutional and private sponsors who supported us to organize this event:

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Université de Haute-Alsace



Swiss Chemical Society



SCS
Swiss Chemical
Society

European Photochemistry Association



ITI HiFunMat



Centre National de la Recherche Scientifique





Scientific Program

Monday 15 mai 2023

13h00	13h45	Welcome	
13h45	14h00	Introductory remarks	
14h00	14h45	K1	Jovana Millic Enhanced Functionality of Hybrid Materials in Photovoltaics
14h45	15h15	I1	Christoph Kerzig One UV photon or two blue photons, that is the question
15h15	15h30	O1	Ricardo J. Fernández-Terán Ultrafast 2D-IR Spectroelectrochemistry of Transition Metal Complexes: One Electron Makes a Big Difference
15h30	15h45	O2	Gregor Jung Intermediates of the Excited-state proton transfer
15h45	16h00	O3	Christophe Humbert Quantum efficiency of excitonic enhancement in nanosensors by rainbow nonlinear optical spectroscopy
16h00	16h15	O4	Gilles Lemercier Excited states of 1,10-Phenanthroline derivatives and related RU(II) (nano-)edifices for potential applications
16h15	16h45	Coffee Break	
16h45	17h15	I2	Chloé Grazon From Quantum Dots to Fluorescent Organic Nanoparticles: bright nanotools for biosensing
17h15	17h30	O5	Alexandre Furstenberg Probing hydration and molecular order locally and quantitatively with fluorophores
17h30	17h45	O6	Marion Cranney Reversible photoisomerization within a 2D self-assembled layer of diarylethene molecules on HOPG
17h45	18h00	O7	Riccardo Ossanna CAP-PHOTOAC: Control of the optical absorption properties of nanovectors for photoacoustic imaging
18h00	18h15	O8	Julien Malletroit Steady-state and photokinetic spectroscopy to reveal negative photochromic secrets of DASA compounds
18h15	18h30	O9	Estefanía Sucre-Rosales Kinetic analysis of the Symmetry Breaking Charge Separation process in a PDI-based Cage
18h30	18h45	O10	Prescillia Nicolas New tetrasubstituted chiral bipyrimidine actives for non-linear optics
18h45	21h00	Poster session#1	
19h00	22h00	Cocktail/Dinner	



Tuesday 16 mai 2023

8h45	9h30	K2 Stefan Hecht	Illuminating Materials, Devices, and Manufacturing with Photoswitches
9h30	9h45	O11 Bernd Strehmel	Photocatalysts Derived from Biomass as Used for Free-radical Photopolymerization, photo-ATRP and Cleaning of Waste Water Complement a New Concept of Sustainable Photochemistry
9h45	10h00	O12 Ainhoa Oilden-Sanchez	Energy transfer processes within Mg-doped ITQ-51 structure channels
10h00	10h15	O13 Qunying Wang	Photophysical Properties and Photochemical Performance of Cyanines Enable Activated Photoinduced Electron Transfer to Initiate Photopolymerization between 700-1100 nm
10h15	10h30	O14 Elena Ishow	Photoswitchable organic nanoparticles toward bioimaging
10h30	10h35	Bruno Volpe	IDIL
10h35	11h00	Coffee Break	
11h00	11h30	I3 Malte Oppermann	Molecules in motion: Capturing and controlling molecular dynamics through chirality
11h30	11h45	O15 Karine Loublere	Combining LED-driven photochemistry and Rose Bengal-anchored polymer colloids as an efficient strategy for carrying out photooxygenation process
11h45	12h00	O16 Marine Labro	Photo-generated diazonia for an anticancer therapy using light
12h00	12h15	O17 Nawel Goual	Design and characterization of red-shifted photochromic molecules
12h15	12h30	O18 Liudmil Antonov	Proton Cranes: What they mean, how they operate
12h30	12h45	O19 Peter Sebej	Structure-properties relationships in cyclic and linear fluorophores: two examples
12h45	14h00	Lunch break	poster session#2
14h00	14h30	I4 Claudia Blizzari	Molecular photo-driven CO2 reduction by earth-abundant systems
14h30	14h45	O20 Monica Martinez-Aguirre	Heterogeneous photoredox reactions and recyclability of an iridium(III) photocatalyst
14h45	15h00	O21 Krystyna Herasymenko	Ultrafast excited state dynamics of the archae-rhodopsin 3 and its mutants
15h00	15h15	O22 Mate Kurucz	Ultrafast spectroscopy of semi-transparent dye-sensitized solar cells
15h15	15h30	O23 Michael Karnahl	Heteroleptic Copper(I) Complexes: Design Strategies, Excited State Properties and Photocatalytic Applications
15h30	15h45	O24 Amira Gharbi	Ultra-fast Energy transfer dynamics in dye-doped organic nanoparticles
15h45	16h00	O25 Iago Modenez	Photoinduced intramolecular electron and energy transfer in a photosensitizer-modified laccase
16h00	16h30	Coffee Break	
16h30	17h00	I5 Ludovic Favereau	Chirality in molecular materials and related photophysical properties
17h00	17h15	O26 Jean Rouillon	Breaking the Resolution Limit in Two-Photon Microscopy Using Molecular Photoswitches
17h15	17h30	O27 Philipp Sikora	Excited state energy landscape of phosphorescent group 14 complexes
17h30	17h45	O28 Saul Garcia-Orrit	Panchromatic antenna induced by nanographene decoration in Ni-porphyrin
17h45	18h00	O29 Mónica Martínez-Junquera	Multi-stimuli responsive chromic cyclometalated Pt(II) complexes
18h00	18h15	O30 Raul Losantos	Unravelling the photoprotection mechanism of synthetic MAA analogues
18h15	18h30	O31 Corentin Bellanger	How Do Phosphiranium Ylides React with Carboxylic Acids? Synthetic Scope and Mechanism.
18h30	21h00	Poster session#3	
19h00	22h00	Cocktail/Dinner	



Wednesday 17 mai 2023

8h45	9h30	K3	Murielle Chavarot-Kerlidou	Fundamental challenges in the design of performant dye-sensitized photocathodes for solar fuels production
9h30	9h45	O32	Albert Ruggl	Good Kobolds: heptacoordinate Co(II) catalysts for hydrogen evolution
9h45	10h00	O33	Kalina Peneva	Design of noble metal-free perylene photosensitizers and their integration in soft matter matrices for light driven hydrogen evolution
10h00	10h15	O34	Daniel Cruz	Time-Resolved Spectroscopic Depiction of Photoinduced Electron Transfers in a Perfluorinated Zn-Porphyrin Sensitizer
10h15	10h30	O35	Federico Droghetti	CO ₂ Reduction in Organic/Water Mixtures with Heptacoordinated Polypyridine Complexes
10h30	11h00	Coffee Break		
11h00	11h30	I6	Dominik Wöll	Super-resolution fluorescence imaging of microgels, New insights into their structure and properties
11h30	11h45	O36	Norbert Hoffmann	Photocycloadditions with lignin derived aromatic compounds
11h45	12h00	O37	Attila Demeter	Some interesting features of photoreduction kinetics of benzophenone
12h00	12h15	O38	Nicolas Fournier Le Ray	From molecular engineering to 3D functional materials for metal cations detection
12h15	12h30	O39	Marie Le Dot	Low-energy consuming initiating system based on a synergistic approach for the polymerization of Elium® thermoplastic resins
12h30	14h00	Lunch break		
14h00	14h15	O40	Gurkan Kesan	Influence of external voltage on excited state dynamics of 8'-apo-beta-carotenal
14h15	14h30	O41	Julien Eng	Joint Experimental and Theoretical Investigation of Excited State Vibrational Coherences in Mn Single Molecule Magnets
14h30	14h45	O42	Yixuan Li	Exploring Anti-Kasha Fluorescence in Azulene Derivatives for Proton Sensing Applications
14h45	15h00	O43	Asma Hasil	Pas de Deux of a nitrosyl Couple: Synchronous Photoswitching from a Double-Linear to a Double-Bent in a metal dinitrosyl photoinduced linkage isomer
15h00	15h30	Concluding remarks - Awards ceremony		

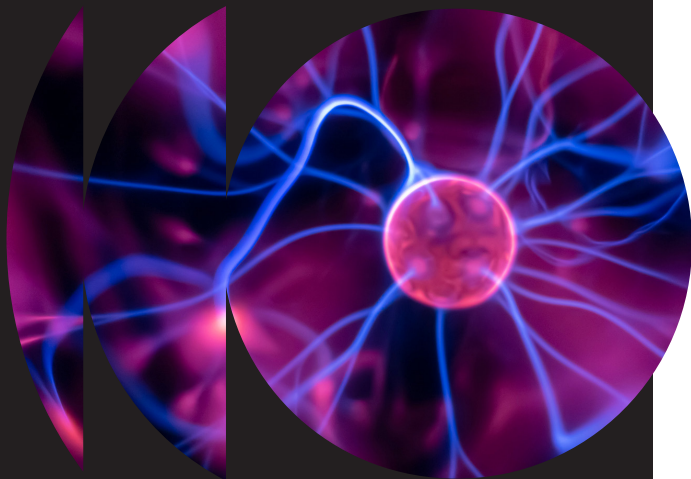


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At a Glance

Wavelength range: Custom and preconfigured options within 200-1100 nm

Optical resolution: 0.14-7.7 nm FWHM (depends on configuration)

Integration time: 8 ms-60 minutes

System SNR: 1000:1 (single acquisition)

Dynamic range: 85,000 (typical)

Stray light: <0.08% at 600 nm; 0.4% at 435 nm

Buffering: 15,000 spectra

TEC: Cooling from -40 °C to +50 °C

Interchangeable slits: Multiple widths from 5 µm-200 µm; SMA bulkhead with no slit also an option

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NEW QE PRO SPECTROMETER MODELS

QE Pro model:	QE Pro UV-Vis	QE Pro Vis-NIR	QE Pro XR
Wavelength range:	200-775 nm	350-925 nm	200-950 nm
Entrance aperture:	10 µm	10 µm	10 µm
Optical resolution (FWHM):	~1.2 nm	~1.2 nm	~1.6 nm
Order-sorting filter:	Yes	Yes	Yes
Best for:	General-purpose and low light applications	General-purpose and low light applications	High sensitivity over wide range
Example applications:	Fluorescence of proteins, dyes, biological samples	Specular and diffuse reflectance of materials	Solar irradiance measurements; blood and tissue analysis

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The *QE Pro* has a thermoelectric cooling (TEC) device to control the temperature of its detector, dramatically reducing the effects of thermal noise and improving the overall stability of the spectrometer during long-term operation. The TEC device holds data stability to 4 dark counts over a 50 °C ambient temperature range, giving users high quality data. This stability performance makes the *QE Pro* ideal for demanding online and at-line quality control measurements, which can be susceptible to environmental and temperature changes.



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Mulhouse
15-17 May 2023

Abstracts

Keynotes

Multifunctionality of Hybrid Materials in Photovoltaics

Jovana V. Milić

¹Adolphe Merkle Institute, University of Fribourg, Switzerland

Email: jovana.milic@unifr.ch

Hybrid organic-inorganic materials are increasingly relevant for emerging energy technologies. In particular, metal halide perovskites have become one of the leading semiconductors for solar-to-electric energy conversion in photovoltaics.¹⁻² However, their operational instability hinders practical applications. While this can, to an extent, be overcome by incorporating organic moieties within hybrid perovskite frameworks that form low-dimensional architectures with superior operational stabilities, their electronically insulating character often compromises the resulting photovoltaic performances.²⁻³ This issue will be addressed by discussing the capacity of supramolecular engineering in the design of adaptive bio-inspired materials² and the use of (photo)electroactive organic species to enhance the functionality of hybrid perovskites by enabling control in response to external stimuli,³ such as voltage bias,⁴ light,⁵ and pressure,⁶ opening a path toward multifunctional materials and smart photovoltaics.

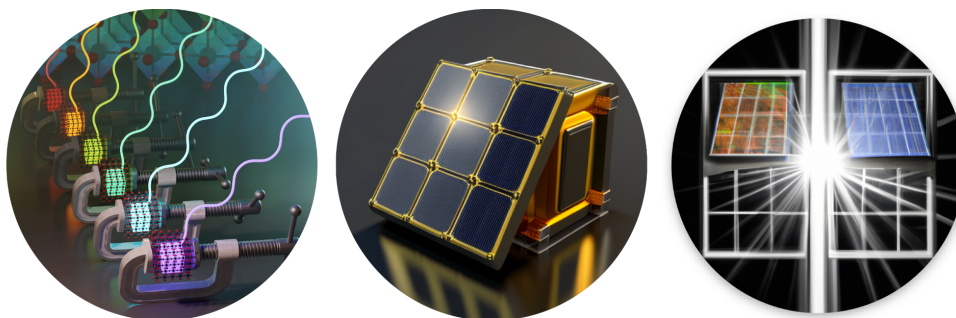


Figure: Schematic representation of stimuli-responsive hybrid perovskite materials (left) toward a new generation of solar cells in smart photovoltaics (right; image design assisted by AI, Midjourney and DALL-E).

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Acknowledgments

The work presented is the result of a collaborative effort across research groups and institutions, in particular at the Adolphe Merkle Institute of the University of Fribourg, EPFL, and PSI in Switzerland, Max Planck Institute for Solid-State Research in Germany, and AMOLF in The Netherlands, as detailed in the references. The speaker is grateful to collaborators, co-workers, and funding support by the Swiss National Science Foundation project, Adolphe Merkle Institute, and NCCR Bio-Inspired Materials.

Illuminating Materials, Devices, and Manufacturing with Photoswitches

Stefan Hecht^{1,2*}

¹ Humboldt University, Dept. of Chemistry & Center for the Science of Materials Berlin, Berlin, Germany

² DWI – Leibniz-Institute for Interactive Materials, Aachen, Germany

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Using an external light stimulus to control and power advanced materials and devices thereof in a dynamic fashion with superior spatial and temporal resolution offers tremendous opportunities. In this context, molecular photoswitches that undergo reversible changes upon illumination have become key ingredients.^{1,2} However, to develop these systems into high-performing materials and practical applications the switching processes have to be highly efficient and reliable. Both criteria are stringent and necessitate continuing optimization of key parameters, involving spectral separation and selective addressability in attractive wavelength regions that enable sufficient light penetration, high quantum yields for switching in both directions, enhanced (photo)chemical resistance enabling highly repetitive switching without fatigue, among others. Importantly, the photoswitchable systems of choice have to undergo significant changes of a physicochemical property of choice in order to maximize its overall achievable modulation. This presentation will briefly highlight selected examples from our laboratory to illustrate how progress in molecular design can be directly translated into materials innovation, ranging from remote-controlled (self)healing films³ and rubbers⁴ over photoactuating films⁵ and coatings to various optically gated electronic devices in transistors,⁶ memories,⁷ and displays.⁸ Moreover, we have developed photoswitchable photoinitiators that form the basis for a new volumetric 3D printing method – xolography – that we have recently developed.⁹ *Fiat lux – let there be light!*

Acknowledgements

I am indebted to the many dedicated coworkers and committed collaborators. Moreover, generous support by a variety of funding agencies, in particular the ERC and the DFG, is gratefully acknowledged.

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FUNDAMENTAL CHALLENGES IN THE DESIGN OF PERFORMANT DYE-SENSITIZED PHOTOCATHODES FOR SOLAR FUELS PRODUCTION

M. Chavarot-Kerlidou^{1,*}

¹Univ. Grenoble Alpes, CNRS, CEA, IRIG, Laboratoire de Chimie et Biologie des Métaux, 38000 Grenoble, France.

Email: murielle.chavarot-kerlidou@cea.fr

The conversion and storage of solar energy into a fuel such as hydrogen H₂ is the subject of intensive research efforts in the field of artificial photosynthesis. To achieve sunlight-driven water splitting, the integration of molecular H₂-evolving catalysts into photoelectrochemical cells represents a promising, yet challenging strategy.^[1-2] Our contribution to the design of functional H₂-evolving dye-sensitized NiO photocathodes based on covalent dye-catalyst assemblies will be presented.^[3-8] A special focus will be made on the investigation of the electron transfer dynamics at the NiO interface, thanks to a spectroelectrochemical setup allowing to record transient absorption spectra at the operando potential. These measurements, together with some post-operando characterizations of the sensitized films, provide key insights into the factors affecting the performances of these dye-sensitized photocathodes^[7-8] as well as guidelines to build more robust and performant devices.

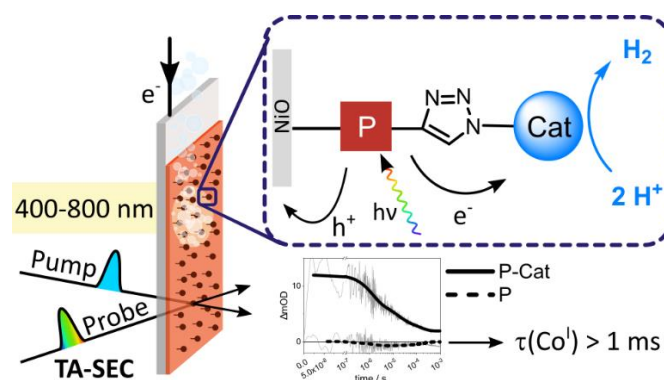


Figure: Schematic presentation of the hydrogen-evolving NiO photocathodes sensitized with covalent dye-catalyst assemblies and of the transient-absorption spectroelectrochemical measurements carried out in these studies.

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French, Swiss and German Conference
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Abstracts

Invited

One UV photon or two blue photons, that is the question

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Several challenging photoreactions require UV light and cannot be driven by one visible photon for thermodynamic reasons. With the aim in mind to replace inefficient UV light sources, we are working on different strategies to pool the energy of two visible photons for achieving similar photochemical reactivities as obtained upon direct (one-photon) UV excitation.[1,2] The conversion of visible light into high-energy UV photons via sensitized triplet-triplet annihilation upconversion (TTA-UC) could pave the way for several energy-demanding applications in the context of photocatalysis.[2] However, only a few annihilator chromophores for Vis-to-UV upconversion are known and the recent limit for the excited-state energy of the UV emitter in TTA-UC schemes was below 4 eV, i.e., in the spectral region (> 310 nm) where the sun still provides a considerable photon flux (Figure 1b). By combining molecular design, time-resolved optical spectroscopy and lab-scale irradiation experiments, we have developed tailor-made sensitizers and aqueous upconversion systems producing high-energy singlet states.[3-5] These states are capable of decomposing a persistent ammonium compound as typical water pollutant with a conventional blue LED. Moreover, we are working on the efficient generation of highly energetic UV light, whose generation would otherwise require environmentally harmful mercury lamps. Very recently, the first blue-light driven upconversion systems with excited annihilator singlets beyond 4 eV were introduced by our group,[6,7] laying the grounds for further bond activation applications under mild conditions with visible light as energy input (Figure 1a).

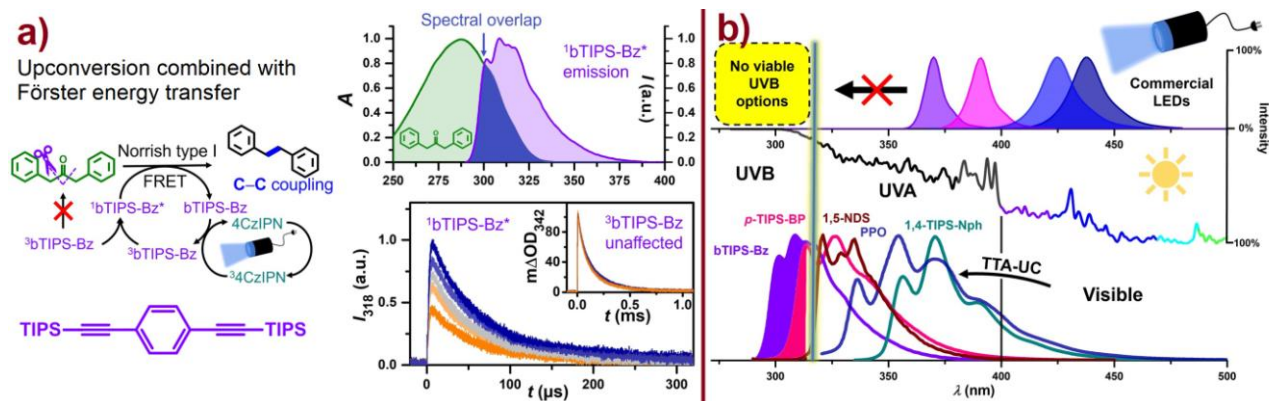


Figure 1: Photon upconversion systems and applications. a) FRET activation of carbonyl compounds via upconversion and mechanistic studies, b) UV annihilator emission and comparison with conventional light sources.

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From Quantum Dots to Fluorescent Organic Nanoparticles: bright nanotools for biosensing

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Förster resonance energy transfer (FRET) is a widely used and an ideal transduction modality for fluorescent based biosensors as it offers high signal to noise with a visibly detectable signal. While intense efforts are ongoing to improve the limit of detection and dynamic range of biosensors based on biomolecule optimization, the nature of and relative location of the dye remain understudied.

Herein, the first part of the presentation will be dedicated to a comparison of the nature of the dye, *i.e.*, organic fluorophore (Cy5 or Texas Red) vs inorganic nanoparticle (QD) and the position of the FRET donor or acceptor on the bioreceptor.^{1,2} Using a recently discovered transcription factor (TF) – DNA biosensor for progesterone³, the four different biosensor configurations are examined and the quantum yield, lifetime, FRET efficiency, IC50, and limit of detection are reported. The key molecular parameters driving the sensor performances in each biosensor configuration are thus identified and a set of design parameters is provided to enable one to select the fluorophore system for their future FRET assays and new diagnostic devices.

In a second part of the talk, Fluorescent organic nanoparticles (Dye-FONs)⁴ will be introduced as metal-free alternative to the QDs, while maintaining a comparable brightness per volume. Dye-FONs are single-component Fluorescent Organic Nanoparticles obtained from the nanoprecipitation of dedicated hydrophobic organic dyes assembled in water. Despite the growing interest in dye-FONs for various biological applications⁵, the strategies deployed to functionalize their surface and to use it as biosensors are still very limited. Current options to obtain fonctionnalisable FONs are mainly to perform the nanoprecipitation of the dye concomitantly with an amphiphilic copolymer, or to coat the FONs with a polymer after the nanoprecipitation. However, when affecting these two approaches, the polymer on the FON's surface increases the nanoparticles' hydrodynamic diameter, which can be detrimental when developing FRET-type biosensors where the sensing dye has to be in close proximity to the fluorescent nanoparticle. To overcome those limitations, we propose an original approach based on direct dye-functionalization. As such, original maleimides push-pull hydrophobic dyes are synthesized and nanoprecipitated to directly obtain fonctionnalisable nanoparticles in water. The efficient surface grafting with a thiolated molecule is proven using the well-known bio-active biotin.

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Molecules in motion: Capturing and controlling molecular dynamics through chirality

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The ability to follow changes in molecular structure during a chemical reaction or biological activity has been a dream of scientists for decades. However, resolving the molecular motion that drives the fastest (bio-)chemical processes has remained a formidable challenge in their native solution phase, where even established methods reach important limitations: nuclear magnetic resonance is limited to millisecond real-time resolution while time-resolved X-Ray scattering requires large-scale free-electron laser facilities.

A promising laboratory-based alternative is circular dichroism (CD) spectroscopy, which measures the absorption difference of left- and right-handed circularly polarized light in chiral molecules. CD is especially attractive in the far and middle ultraviolet (UV) <300 nm, where it is routinely used to characterise the chiral equilibrium structures of proteins, DNA and chiral organic complexes. However, taking this technique to the time-domain has remained a challenge for over three decades, with only few isolated reports with sub-nanosecond time-resolution [1].

In this talk, I will present a novel time-resolved CD spectrometer that combines ultra-sensitive broadband detection in the deep-UV (250-370 nm) with sub-picosecond time-resolution [2]. This has finally opened the path to measure the CD spectra of photoexcited chiral molecules in solution and to follow the encoded structural dynamics with ultrafast time-resolution. In my talk I will illustrate these exciting new experimental capabilities with an investigation of Fe(II) spin-crossover complexes, where – despite decades of research – the relaxation mechanism of their excited high-spin state has remained unresolved. By combining ultrafast CD with transient absorption and anisotropy measurements of a prototypical chiral Fe(II) complex, we now show that the spin-relaxation mechanism involves a torsional twisting mode that breaks the chiral symmetry of the compound [3]. Quite remarkably, suppressing the vibrational population of this mode then slows down the spin-relaxation.

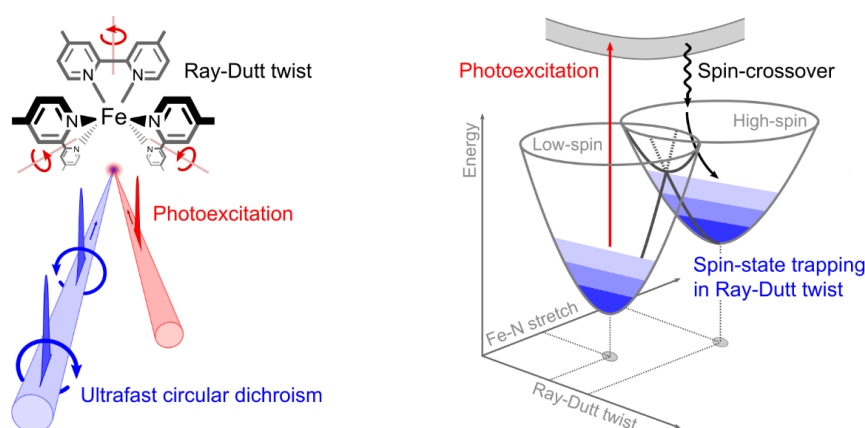


Figure: Ultrafast circular dichroism uses circularly polarized laser pulses to probe the chiral properties of the photoexcited high-spin state, revealing that its decay is driven by the symmetry-breaking mode, called the Ray-Dutt twist (left). The spin-crossover mechanism of Fe(II) complexes thus involves two reaction coordinates (right).

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Molecular photo-driven CO₂ reduction by earth-abundant systems

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Renewable energies and resources should be exploited in order to tackle contemporary challenges, such as climate change and depletion of earth resources. In particular, learning how to efficiently use solar light for energetic human needs is a must for sustainable development of processes. [1] Besides solar energy conversion into thermal or electrical energy, [2] one of the best ways to store energy is in the form of fuels, namely in chemical bonds. [3] The formation of highly energetic molecules from CO₂ as starting material is highly desirable. The use of transition metal complexes is promising because their photocatalytic activity and efficiency. Nevertheless, in terms of applicability, these catalysts should be readily available and cost-effective; thus, earth-abundant materials are highly desired. [4]

Novel mononuclear and binuclear Cu(I) complexes have been prepared with suitable photophysical and electrochemical properties by modification of their diimine ligand, and were used as photosensitizers, [5] In particular, their use in photocatalytic systems to reduce CO₂ to CO, under blue light in combination with the catalyst [Ni(cyclam)]Cl₂ was tested. To the best of our knowledge, this was the first example reported of Cu(I)-based photosensitizers with this kind of catalyst. Moreover, the TONs obtained (up to 8) are in line with those results produced in previous works with noble-metal based photosensitizers. Recently, we focused on developing new CO₂ reduction catalysts based on Fe(II).[6] We will show a new heteroleptic Fe(II) complex based on the *N,N,N*-pincer ligand 2,6-bis(4'-phenyl-1',2',3'-triazol-1-yl-methyl)pyridine. By comparing its activity to its cobalt analogue and the corresponding homoleptic iron- and cobalt-based complexes, we reveal that in MeCN the iron complexes are remarkably more effective than the cobalt analogues. The new catalyst shows considerable activity as in the photo-driven catalysis induced by a Cu(II)-photosensitizer, giving CO with a TON of 576 and a quantum yield of up to 7 %. Competitive H₂ formation leads to syngas generation.

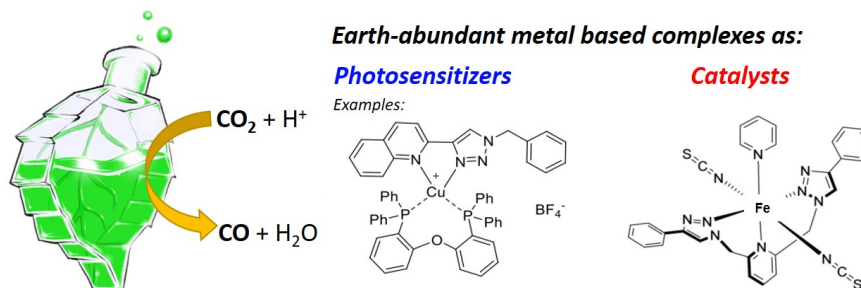


Figure : Photo-driven CO₂ conversion as artificial photosynthesis. The structures of a Cu(I)-based photosensitizer and a Fe(II)-based catalyst were presented.

Acknowledgements

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Chirality in molecular materials and related photophysical properties

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Chiral π -conjugated materials have recently emerged as a promising direction in material science due to their specific interaction with CP-light and the spin of electron, impacting several domains of applications such as organic light-emitting diodes (OLEDs) for instance, and spintronics.¹

In this presentation, I will present our contributions regarding this area of research, with firstly the design of covalent and intermolecular chiral luminophores displaying thermally activated delayed fluorescence (TADF) for developing OLEDs with polarized electroluminescence.²

I will also illustrate our recent attempts to develop persistent organic chiral mono- and diradicals in which the energy of the singly occupied molecular orbital (SOMO) is below the highest doubly occupied molecular one (HOMO) level, and the impact of these peculiar orbital energetics on both the electronic and photophysical properties of these radicals.³

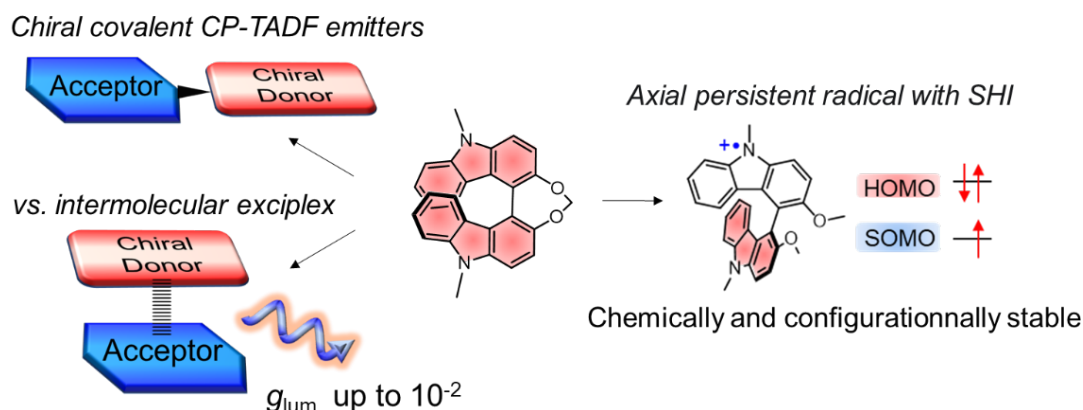


Figure: Chemical structure of chiral bicarbazole compound with an illustration of the approaches explored to develop CP-TADF emitters (left), and a schematic illustration of the SOMO-HOMO Inversion (SHI) obtained for the electronic configuration of the corresponding chiral cationic bicarbazole radical (right).

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Super-resolution fluorescence imaging of microgels – New insights into their structure and properties

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Super-resolution fluorescence microscopy techniques are constantly improving and creating new opportunities to explore the nanoscale. The methods originally developed for biological systems have gained importance also in materials and polymer science. Localization-based super-resolution fluorescence microscopy methods were applied to address different topics concerning stimuli-responsive microgels,[1,2] an interesting class of hydrogel particles with high potential for many applications ((bio-)catalysis, drug-delivery, tissue engineering, sensors, advanced bioimaging, extraction processes, responsive membranes, etc.). As shown in the Fig. 1, super-resolution fluorescence microscopy assisted us in analyzing compartmentalization,[3] cross-linking,[4] and local environment[5] inside microgels, as well as the deformation of microgels at different surfaces.[6]

The talk will outline a selection of our results and discuss the power of super-resolution microscopy to address relevant topics in microgels and, generally, in polymer science.

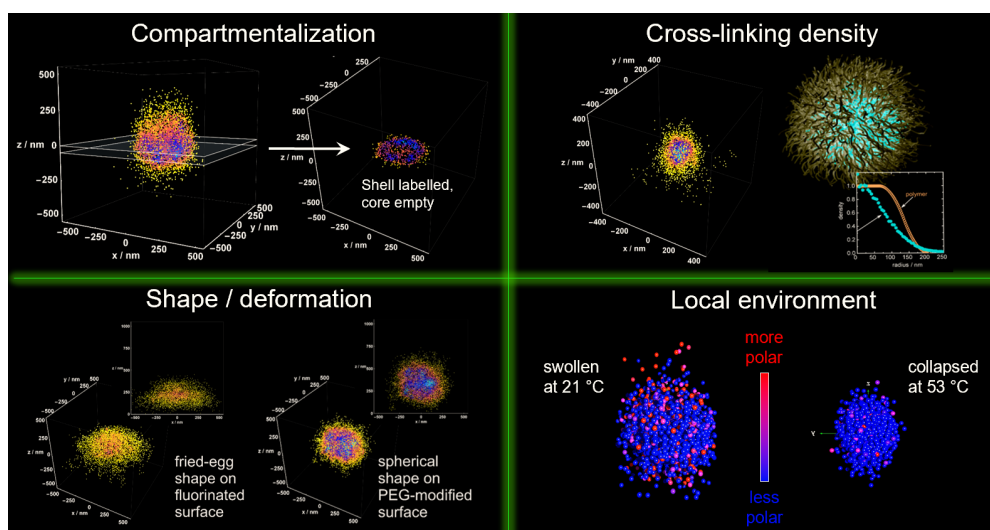


Figure 1: Own examples of super-resolution fluorescence imaging of microgels.

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Abstracts

Orals



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O3	Christophe Humbert	Quantum efficiency of excitonic enhancement in nanosensors by rainbow nonlinear optical spectroscopy
O4	Gilles Lemerrier	Excited states of 1,10-Phenanthroline derivatives and related RU(II) (nano-)edifices for potential applications
O5	Alexandre Furstenberg	Probing hydration and molecular order locally and quantitatively with fluorophores
O6	Marion Cranney	Reversible photoisomerization within a 2D self-assembled layer of diarylethene molecules on HOPG
O7	Riccardo Ossanna	CAP-PHOTOAC: Control of the optical absorption properties of nanovectors for photoacoustic imaging
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O21	Krystyna Herasymenko	Ultrafast excited state dynamics of the archae-rhodopsin 3 and its mutants
O22	Mate Kurucz	Ultrafast spectroscopy of semi-transparent dye-sensitized solar cells
O23	Michael Karnahl	Heteroleptic Copper(I) Complexes: Design Strategies, Excited State Properties and Photocatalytic Applications
O24	Amira Gharbi	Ultra-fast Energy transfer dynamics in dye-doped organic nanoparticles



025	Iago Modenez	Photoinduced intramolecular electron and energy transfer in a photosensitizer-modified laccase
026	Jean Rouillon	Breaking the Resolution Limit in Two-Photon Microscopy Using Molecular Photoswitches
027	Philipp Sikora	Excited state energy landscape of phosphorescent group 14 complexes
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030	Raul Losantos	Unravelling the photoprotection mechanism of synthetic MAA analogues
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032	Albert Ruggi	Good Kobolds: heptacoordinate Co(II) catalysts for hydrogen evolution
033	Kalina Peneva	Design of noble metal-free perylene photosensitizers and their integration in soft matter matrices for light driven hydrogen evolution
034	Daniel Cruz	Time-Resolved Spectroscopic Depiction of Photoinduced Electron Transfers in a Perfluorinated Zn-Porphyrin Sensitizer
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037	Attila Demeter	Some interesting features of photoreduction kinetics of benzophenone
038	Nicolas Fournier Le Ray	From molecular engineering to 3D functional materials for metal cations detection
039	Marie Le Dot	Low-energy consuming initiating system based on a synergistic approach for the polymerization of Elium® thermoplastic resins
040	Gurkan Kesan	Influence of external voltage on excited state dynamics of 8'-apo-beta-carotenal
041	Julien Eng	Joint Experimental and Theoretical Investigation of Excited State Vibrational Coherences in Mn Single Molecule Magnets
042	Yixuan Li	Exploring Anti-Kasha Fluorescence in Azulene Derivatives for Proton Sensing Applications
043	Asma Hasil	Pas de Deux of a nitrosyl Couple: Synchronous Photoswitching from a Double-Linear to a Double-Bent in a metal dinitrosyl photoinduced linkage isomer

Ultrafast 2D-IR Spectroelectrochemistry of Transition Metal Complexes: One Electron Makes a Big Difference

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In this talk, I will discuss our recent results from two-dimensional infrared spectroelectrochemistry (2DIR SEC) in two model systems: (i) transition metal hydridocarbonyl complexes; and (ii) transition metal polypyridyl(azido) complexes. In the first case, we observe a blue shift of both absorption bands upon oxidation of the parent $[\text{Hlr}^{\text{I}}(\text{CO})(\text{PPh}_3)_3]$ complex, and a retention of the coupling between the M–H and $\text{M}(\text{C}\equiv\text{O})$ stretching modes (Fig. 1a).¹ A change in the 2D line shapes is also evidenced, pointing towards an increased interaction with the solvent/electrolyte mixture. In the second class, exemplified by $[\text{Fe}^{\text{III}}(\text{terpy})(\text{N}_3)_3]$ (Fig. 1b), we observe upon reduction of the complex a systematic blue shift of all bands in non-coordinating solvents, whilst the situation becomes less clear in coordinating solvents (e.g. THF).

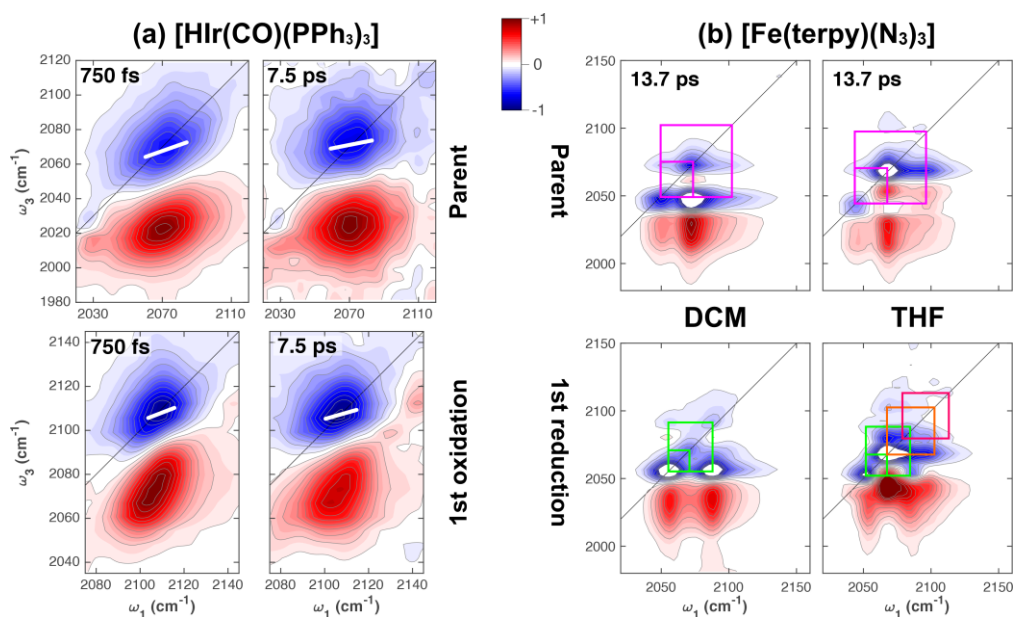


Figure 1: 2DIR SEC spectra of hydridocarbonyl (a) and azido (b) complexes as a function of the oxidation state and solvent. The squares in (b) reveal the couplings between the sets of vibrational modes. terpy = 2,2':6',2''-terpyridine.

In conjunction with density functional theory (DFT) calculations, these results illustrate how the structure and dynamics of these complexes change upon redox reactions and as a function of solvent properties. The understanding of these differences is vital for the development of robust photocatalytic systems, where these complexes will engage in complicated electron and proton-coupled electron transfer chains.

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INTERMEDIATES OF THE EXCITED-STATE PROTON TRANSFER

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Excited-state proton transfer (ESPT) is one of the few photochemical reactions which is compatible with emission. Excitation of an aromatic alcohol can lead to a reversible release of a proton, which then undergoes a chain of sequential proton transfer steps. Each elementary reaction affects the electronic structure of the parent compound and, thus, the transition wavelength. Therefore, fluorescence spectroscopy offers a convenient toolbox for mechanistic investigations, and even single-molecule detection is feasible under beneficial experimental conditions. We synthesized in the past highly fluorescent and photostable so-called photoacids which undergo repeated Förster-cycles of ESPT and ground-state reprotonation in polar protic and aprotic solvents.^[1] Quantum-optical antibunching experiments allowed for assessing the recombination kinetics on the single-molecule level.^[2,3] Chemical modification of the compounds can be exploited for monitoring transition-metal catalyzed chemical conversion of individual molecules.^[4,5]

In my presentation, I will focus on our attempts to catch and characterize intermediates of the ESPT reaction. We recently analyzed the thermodynamics and kinetics of the formation of the hydrogen-bonded ion pair (HBIP), the first intermediate of the reaction chain, by ensemble spectroscopy.^[6,7] The advantage of the ESPT reaction over other chemical transformations is that an individual chemical reaction can repeatedly be probed, and information about environmental heterogeneity can be obtained. Emission spectra in a solid polar, aprotic environment point to a large heterogeneity of the surrounding and may serve as a frozen excerpt of the configuration in solution.

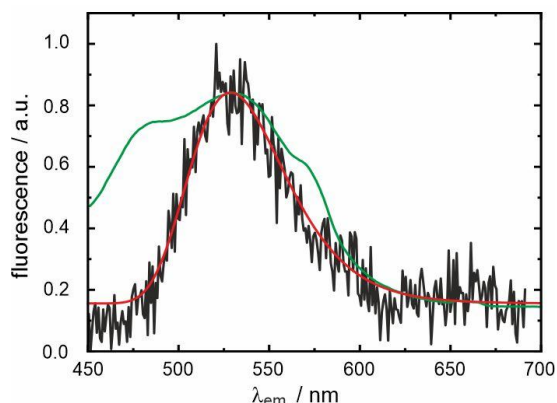


Figure: Emission spectrum of a single pyrenol-derivative in a phosphine oxide matrix (black), together with the ensemble spectrum (green) and the extracted line shape of HBIP from ensemble experiments^[6] (red).

Acknowledgements

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Quantum efficiency of excitonic enhancement in nanosensors by rainbow nonlinear optical spectroscopy

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Quantum dots (QD) constitute a novel generation of fluorescent probes due to their confined size in the 1-10 nm range. In this field, nanosensors sensitivity is of pivotal importance to target biomolecules. We focus here on the grafting of organic ligand-coated CdTe QDs monolayers on glass surfaces to address the environmental problem and cost of nanosensors.¹ QD monolayers samples are pre-characterized by UV-VIS absorption and (Time-resolved) fluorescence emission, evidencing the success of transferring the QD optoelectronic properties from colloidal solution to amine-terminated aliphatic organosilane monolayer-modified glass samples. Moreover, from time-resolved fluorescence spectroscopy, the effect of chemical structure of monolayers are seen from a fast-quenching phenomenon in relation to colloidal QD solution. Afterwards, an advanced surface-specific spectroscopic tool, non-linear optical Two-Colour IR-Visible Sum-Frequency Generation spectroscopy (2C-SFG), is used to probe and evidences the dipolar coupling between QD excitons and their molecular surroundings,² which improves the nanosensor's detection threshold. This electro-optical coupling (inorganic-organic charge transfer) is modelled in an original formalism we developed and based on Feynman loop-diagrams.³

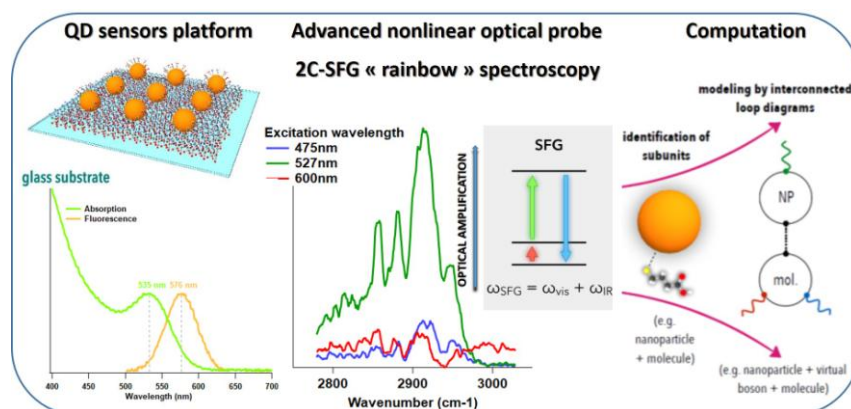


Figure: Sketch of a QD sensors based-platform probed by advanced nonlinear optical 2C-SFG spectroscopy.

Acknowledgements

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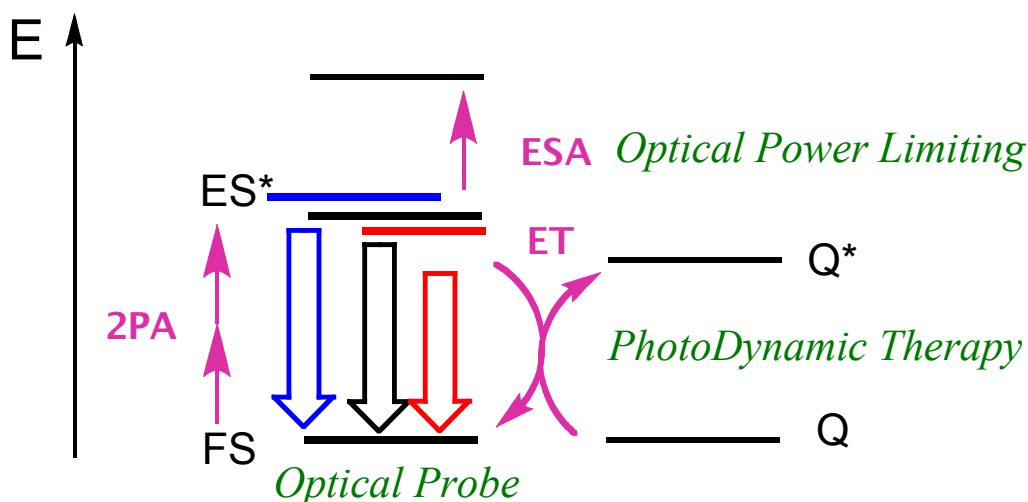
EXCITED-STATES OF 1,10-PHENANTHROLINE DERIVATIVES AND RELATED RU(II) (NANO-)EDIFICES FOR POTENTIAL APPLICATIONS

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The presentation will concern studies in the field of the linear and nonlinear optical properties of 1,10-phenanthroline type ligands and related Ru(II) complexes¹. One- and two-photon induced (2PA) access to ³MLCT excited states will be discussed both in a fundamental interest and in the perspective of potential applications in physics and biology such as (antimicrobial-)photodynamic therapy [(a-)PDT]². The elaboration of associated functionalized surfaces³ and nano-particles⁴ will also be presented and discussed in the main perspective of applications in theranostic⁵. Collaborators of these studies will be cited during the talk and are co-authors of the bibliographic references reported below.



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Probing hydration and molecular order locally and quantitatively with fluorophores

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Most biological processes take place in compartmentalized aqueous environments. Nonetheless, water diffusion across membranes and its dynamics in response to changes in osmolarity, membrane composition, membrane tension, or membrane protein conformation is not understood in detail. We have recently shown that some oxazine fluorophores are selectively sensitive to water and can quantitatively report on the number of water molecules in their contact sphere by measurement of their fluorescence lifetime,[1, 2] while mechanosensitive flipper probes displaying ground-state planarization are designed to specifically sense variations in membrane tension and are compatible with single-molecule imaging.[3] We report in this contribution how such quantitative fluorescent probes can be used to investigate membrane composition, hydration, tension, and dynamics at the nanometer scale using fluorescence lifetime imaging and super-resolution microscopy.

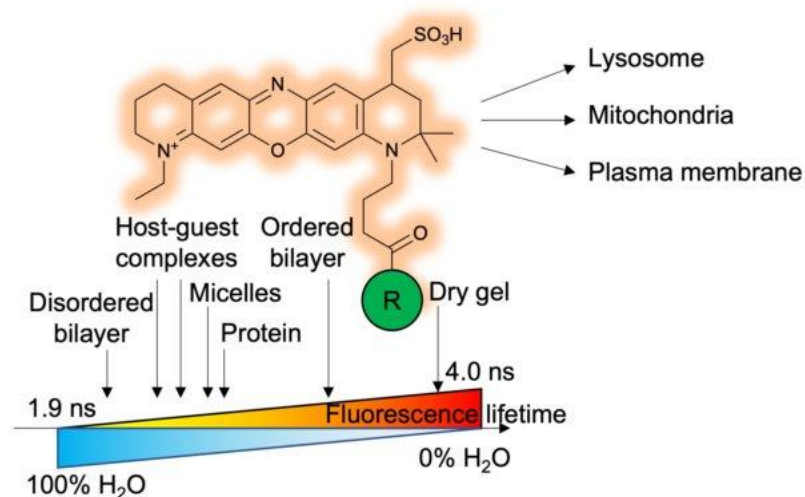


Figure : Modulation of the water content in their direct environment is sensed by red-emitting dyes.

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Reversible photoisomerization within a 2D self-assembled layer of diarylethene molecules on HOPG

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This study comes within the framework of design and study of smart surfaces. They are based on the self-assembly of functionalized molecules on a substrate, that will respond in a defined way to an external stimulus. As the use of light to control smart surfaces seems to hold promising prospects [1], diarylethenes [2] are one of the most appropriate functionalized molecules for the achievement and study of smart surfaces.

In this study, we report an in situ reversible photoisomerization within a self-assembled layer of diarylethene molecules on a graphite surface at the solid-liquid interface. To achieve this aim, a new diarylperfluorocyclopentene derivative has been designed and synthesized. Its photophysical properties have been investigated by a UV-visible study in solution, confirming its interesting properties. A submolecularly resolved scanning tunneling microscopy study shows that both open and closed isomers form a self-assembled layer on HOPG at the solid-liquid interface, with markedly different organizations, as seen in the figure below. In situ UV and visible light irradiations lead to reversible isomerizations of the molecular self-assembled layer, without degradation and with a conversion ratio of 100%. Using linearly polarized light, we prove that this reversible photoisomerization occurs within the 2D self-assembled layer and not in solvent coupled to a molecular desorption-readsorption process, which should have hindered dramatically the use of these diarylethenes for potential applications. Indeed, we observe a selective isomerization of the domains of closed molecules according to the direction of polarization of the light. This had already been shown in the case of 3D crystals of diarylethenes, where there was isomerization when the direction of polarization was aligned with the moment of molecular electronic transition [3]. Furthermore, the self-assembly of the closed molecules is improvable by light irradiation, leading to expanding closed domains without thermal treatment of the sample which might damage the molecular layer.

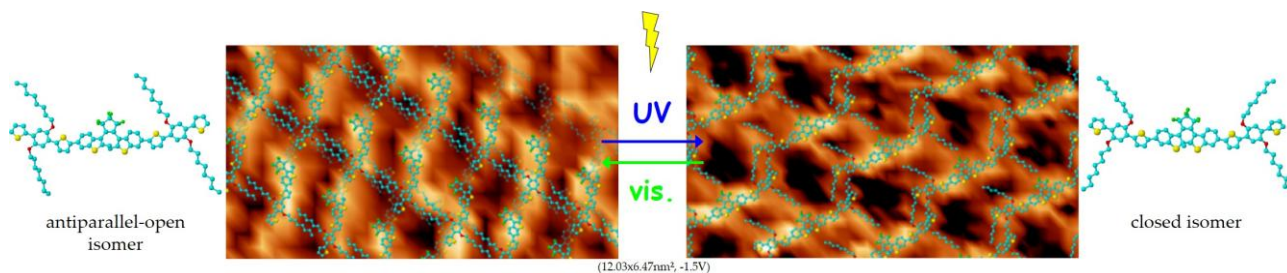


Figure : Results on the self-assembly of diarylethene BT-(TBT)₁ on HOPG dissolved in 1-phenyloctane.

The molecules are able to isomerize reversibly within the self-assembled layer upon exposure to light.

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CAP-PHOTOAC: Control of the optical absorption properties of nanovectors for photoacoustic imaging

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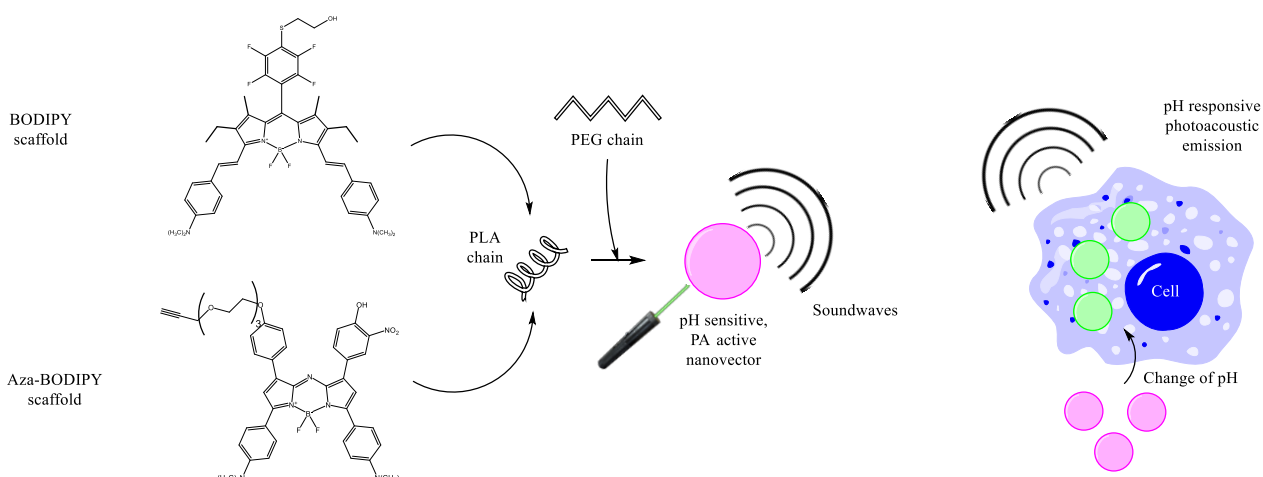
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Optically absorbing structures can generate sound waves via the photoacoustic (PA) effect, which enables high-resolution imaging of molecules or nanoparticles in biological tissues. BODIPY dyes are commonly used as molecular PA agents due to their high absorption coefficient, tunable absorption maxima, and photostability. Past work from our research group¹ has produced a novel BODIPY-based chromophore that, when conjugated to a lactide chain and grafted onto a PEGylated nanoparticle (NP), shows remarkable absorption properties and biocompatibility, making it an excellent platform for PA imaging and drug delivery.

In this study, we aim to develop a stimulus-responsive PA agent by synthesizing and characterizing a pH-sensitive molecule using the aza-BODIPY scaffold. This scaffold has structural similarities to the commonly used BODIPY scaffold and has been employed in the creation of pH-sensitive fluorophores². Our current work involves introducing on a symmetric diphenol-dimethylaniline-aza-BODIPY molecule reported in the literature³ a clickable PEG-handle on one phenol and a nitro group in ortho on the other phenol to modulate its pKa to respond to changes in the biological environment. We plan to conjugate the pH-sensitive aza-BODIPY to previously developed BODIPY-labeled PLA-PEG NPs to create multifunctional NPs that provide control over the optical absorption without adding toxicity. These nanoparticles will be biocompatible and pH-sensitive PA agents that we intend to use to evaluate their intratissue distribution and intracellular uptake kinetics in a murine model of rheumatoid arthritis. Overall, this work aims to showcase the potential of these NVs as a clinically relevant, biocompatible, and photostable platform for personalized medicine and nanomedicine, enabling real-time visualization of drug distribution and patient response.



Acknowledgements

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Steady-state and photokinetic spectroscopy to reveal negative photochromic secrets of DASA compounds

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Under UV-light irradiation, “positive” photochromic molecules can perform a reversible structure modification from a colorless isomer to a colored one¹. During the last few decades, new families of molecules have been studied showing “negative” photochromism, i.e. the most stable isomer is colored, and upon visible light irradiation, the colorless isomer is generated². Those molecules have various applications, such as creating light-responsive nanocarriers³ or phase transfer agent⁴. This work focuses on spectroscopic studies of Donor-Acceptor Stenhouse Adduct (DASA) molecules⁴ (Figure 1a) to understand the photochemical reaction and determine the photophysical properties. Steady-state spectroscopy was carried out in solution to provide the main spectral characteristics. In contrast, photokinetic experiments in the presence or absence of illumination allow for highlighting three major phenomena of the DASA compounds when dissolved in solution (Figure 1b): a “dark equilibrium,” which was also followed by NMR, a “photostationary state” under irradiation (the color is lost), and a “thermal back reaction” in the absence of light (the color is recovered). Fatigue resistance and the impact of the irradiation power are also presented. Thanks to those combined experiments, we can get experimental values of the molar absorption coefficients, the thermal kinetic rates, and the photochromic quantum yields, leading to a better overview of the properties of the molecules.

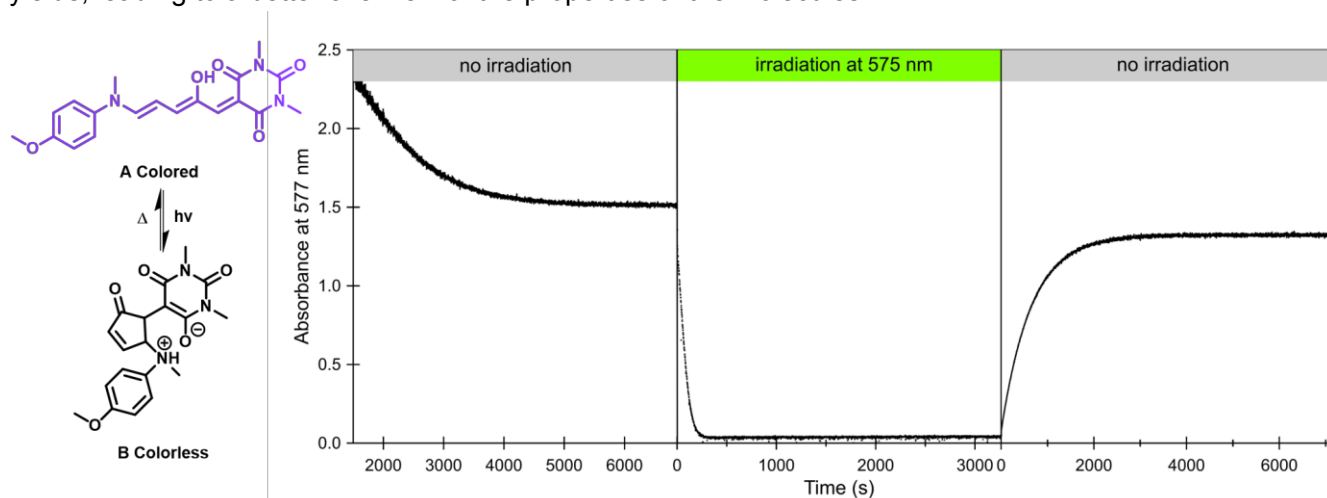


Figure 1: a. Photochromic reaction of a DASA compound investigated in this work. b. Photokinetic experiment showing the three different phenomena of the DASA molecule in solution, with or without irradiation.

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Kinetic analysis of the Symmetry Breaking Charge Separation process in a PDI-based Cage

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In a photoinduced symmetry-breaking charge-separation (SB-CS) process, an electron is transferred between two identical chromophores. This phenomenon has potential applications for solar energy harvesting. Our previous work showed the first example of a cage with delayed fluorescence [1], presumably by a reverse SB-CS process. Using transient electronic absorption spectroscopy (TAS) in Toluene/PhCN mixtures, we have successfully identified the spectral signature of the SB-CS (PDI radical anion and cation) when increasing the solvent polarity. The radical transient bands are absent in low polarity solvent mixtures, which coincides with the destabilization of the CS state which impedes the SB-CS process in this condition.

We analyzed the data using a model consisting an initial solvent relaxation step after excitation to the Franck-Condon excited state, the population/depopulation (equilibria) of the ¹CS state, the S₁ state decay, and the ¹CS state recombination. Since this model involves five kinetic constants, additional constraints were added using the amplitudes and time constants derived from TCSPC fluorescence decays according to an adaptation of Ware's model for exciplexes [2]. This new approach allowed not only to extract distinct Species-Associated Spectra, but also to obtain relevant time constants from a complex scheme that can be used to access the equilibrium constant and the driving force for the SB-CS process while assuring self-consistency between the TAS and TCSPC derived kinetic data.

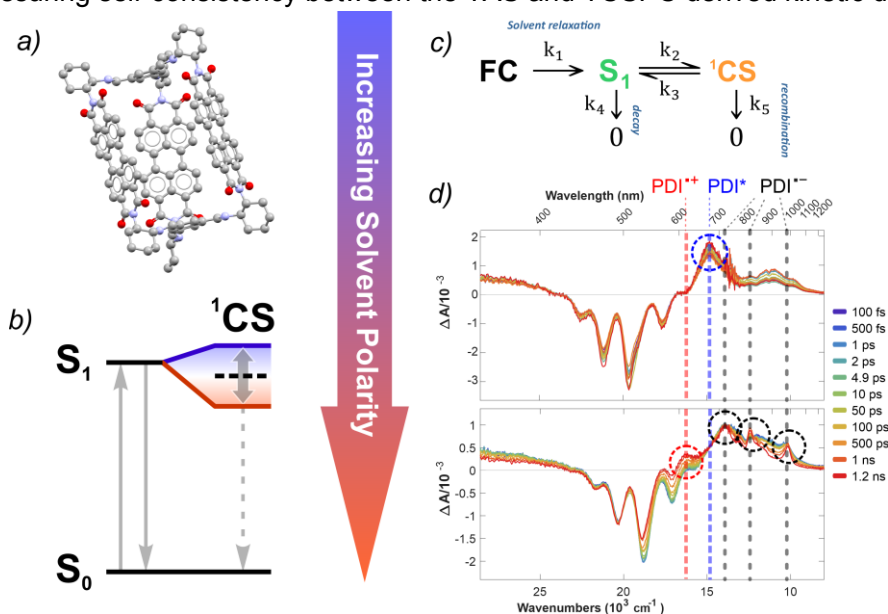


Figure: a) PDI-based Cage, b) Stabilization of the ¹CS state with increasing solvent polarity, c) Comparison between toluene (up) and benzonitrile (bottom) transient absorption spectra. d) Target model scheme

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NEW TETRASUBSTITUTED CHIRAL BIPYRIMIDINE ACTIVES FOR NON-LINEAR OPTICS

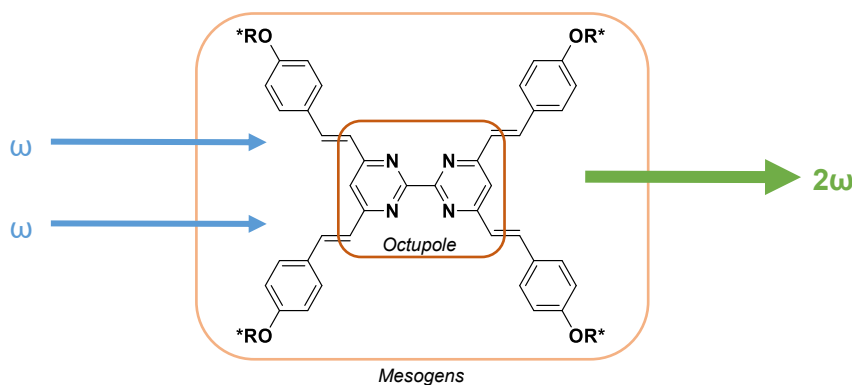
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Non-linear optics (NLO) has developed remarkably since the discovery of intense laser sources¹, particularly for applications in optoelectronics and photonics.² Second harmonic generation (SHG) is a second order NLO phenomenon that requires a molecule with a non-zero dipole moment. In this process, two photons at the fundamental frequency ω are converted into a single photon at the double harmonic frequency 2ω .³



To preserve a good SHG signal in solid state, non-centrosymmetry must also be maintained at the macroscopic level within an ordered structure. In order to obtain non-centrosymmetric solids, in the form of thin films, a strategy has been set up consisting of the synthesis of chiral liquid crystals with an octupolar core.⁴ For this purpose, chiral carbon chains were grafted at the periphery of bipyrимidine molecule of D₂ symmetry. The supramolecular solid state structure shows nematic liquid crystal phase which is comprised of chiral columns. The molecule can be easily processed into large, flexible and thin films with SHG responses competitive to the prototypical inorganic KH₂PO₄ (KDP) crystals.

In this presentation, the synthesis of tetrafunctionalized bipyrимidine core molecules with new chiral pro-mesogenic fragments will be discussed as well as the SHG results.

Keywords: Bipyrимidine, Liquid Crystals, Thin Films, Nonlinear Optic, Chirality

Acknowledgements

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Photocatalysts Derived from Biomass as Used for Free-radical Photopolymerization, photo-ATRP and Cleaning of Waste Water Complement a New Concept of Sustainable Photochemistry

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Biomass derived from lac dye, alginate, cellulose, hemicellulose, and citric acid served as raw material to make the Carbon Nanodots (**CDs**). Some of these materials have received increased attention as photocatalyst in the field of ATRP since 2020[1,2]. Their different origin resulted in different efficiencies for the photo-ATRP using as metal catalyst either (Cu/TPMA)Br₂ or FeBr₃ at the ppm scale. Alternatively, a metal free approach also successfully worked with confined **CDs** obtained from cellulose in a silica confined network. It exhibited a room temperature phosphorescence (RTP) greater than 100 ms. Here, formation of the triplet state connects the system to a metal free photo-ATRP reaction protocol while systems with no efficient triplet formation failed. Alternatively, hydrothermal treatment of furfural available from hemicellulose provided **CDs** with aldehyde groups on the surface. This material reacted with dipyrromethane resulting in porphyrin-based organic network comprising sustainable carbon dots. The low cytotoxicity of the **CDs** was also remarkable. The polymers obtained exhibited a different dispersity of molecular weight depending on the biomass origin of the **CD**. Photocatalysts derived from *Kerria lacca* resulted in the lowest value; that is ≈ 1.1 , using Cu(TPMA)Br₂ in a range of <100 ppm and Ethyl- α -bromo phenylacetate as initiator. This approached numbers of \bar{D} remaining close to the traditional ATRP while other **CDs** resulted in higher values. Furthermore, results obtained demonstrated the use of a sustainable photocatalyst with multiple purpose comprising demethylated lignin (**Fe₃O₄@D-wood**). This was made by treatment of wood and iron oxide. Characterization followed by XRD, UV-Vis, photo-current studies, and electrochemical measurements. This material became subject of photocatalytic explorations for water treatment and material synthesis by radical photopolymerization. Exposure of **Fe₃O₄@D-wood** with artificial sunlight showed an improved activity considering photochemical oxidation of organic pollutants in the presence of H₂O₂. The efficient generation of reactive radicals brought this system also to photopolymerization. Here, radicals based on reactive oxygen species (ROS) generated in the catalytic cycle can be seen as the dominating species to initiate radical polymerization. A mixture of **UDMA** and **TPGDA** showed good reactivity with cumene hydroperoxide (**CHP**). Photocatalyst used for water treatment facilitates reuse for photopolymerization.

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Energy transfer processes within Mg-doped ITQ-51 structure channels

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The combination between photoactive molecules and inorganic structures is of great interest for the development of advanced materials in the field of optics. In this way, the design and proper selection of the components that make up the photoactive hybrid systems are crucial to establish the perfect combination and improve the photophysical properties, such as the fluorescence efficiency. The most important factors to consider in the design are the type (channels or cages) and dimensions of the host nanochannels, and the molecular size and intrinsic properties of the guest dyes.

Particularly, zeotypes with extra-large pore size are attractive because they allow the accommodation of bulky dyes. To this end, this work presents an exhaustive photophysical study of the inorganic structure Mg-doped ITQ-51 [1] that meets the above-mentioned conditions (Figure 1a). To prepare this framework, the structure-directing agent DMAN is employed which results in a material with time-varying properties that fluoresces in the blue range of the visible spectrum by itself (Figure 1b). To extend the action of the material and to mimic processes such as photosynthesis in which FRET energy transfer is essential, two robust laser dyes (Rhodamine 123 and Nile Blue, Figure 1c and Figure 1d respectively) have been coencapsulated together with DMAN in a straightforward process called one-pot synthesis (an efficient method demonstrated in other previous works) [2]. Thus, photoactive systems with emission in the entire visible range have been obtained due to a partial FRET between organic chromophores protected in a rigid matrix of aluminophosphate nature.

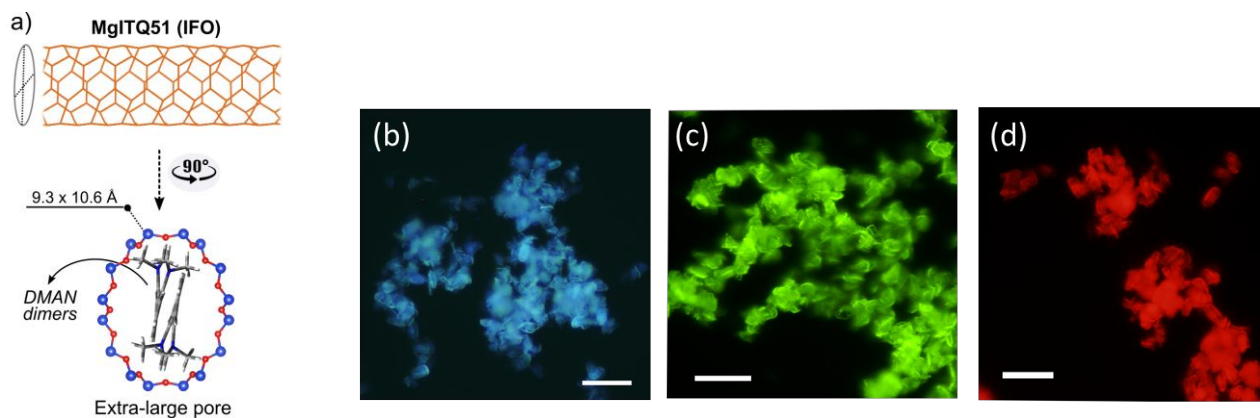


Figure 1: (a) Illustrative representation of the ITQ-51 framework nanochannels and the view of the pore opening by a 90° turn with the allocated DMAN dimers inside; and fluorescence images of dye-MgIFO particles (scale = 20 μm) (b) with DMAN (structure-directing agent), (c) Rhodamine 123 and (d) Nile Blue.

Acknowledgements

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Photophysical Properties and Photochemical Performance of Cyanines Enable Activated Photoinduced Electron Transfer to Initiate Photopolymerization between 700-1100 nm

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A series of cyanine dyes comprising distinct terminal groups, namely benzo-, benzo[e]-, benzo[g]-, and benzo[cd]indolium, were chosen to explore the relation between structural pattern, photophysical properties (fluorescence decay time and quantum yield) and photochemical performance to initiate free radical and/or cationic photopolymerization. Iodonium salts served as co-initiator with the excited state of cyanines in a photoinduced electron transfer (**PET**) protocol. Variation of the connecting methine chain and terminal moieties resulted in distinguished efficiency to generate initiating moieties such as radicals and conjugate acids. Photophysical data (λ_f^{\max} and Φ_f) provided the decay time of excited states (between 25 ps-1.5 ns) and contribution of nonradiative deactivation resulting in generation of additional heat needed within activated photoinduced electron transfer. This worked well with high-intensity sources such as new high-power LED-devices emitting up to 1060 nm^[1].

The terminal group surprisingly showed strong impact on the radiative activation and non-radiative deactivation upon exposure. Here, benzo[cd]indolium derivatives exhibited efficient non-radiative deactivation and therefore nearly quantitative conversion of heat with respect to the absorbed light quanta. This technology of high-power NIR-LED prototypes brings also new impetus into the world of photochemistry under activated **PET** reaction. This reaction only worked in combination with high-intensity sources while low intensity emission failed to start the **PET**. This combination of initiator system could sufficiently initiate free radical photopolymerization of the monomers **UDMA**, **TPGDA** and **TMPTA**. While cyanines based on heptamethine and nonamethine succeeded in the initiation of cationic photopolymerization resulting in significant reactivity. Surprisingly, an enhancement of cationic polymerization occurred in systems based on hybrid photopolymerization as confirmed by real-time FTIR measurements and explorations of mechanical properties of the polymer films characterised by DMA^[2].

Furthermore, the combination of heptamethine cyanine based on the selection with iodonium salt also successfully initiated solidification of sol-gel coatings comprising nanoparticles obtained by silanization following a mechanism of cationic photopolymerization. This resulted in films exhibiting higher T_g than that of UV exposed systems. In addition, the heat generated upon excitation from water soluble heptamethine based cyanine in coatings functioned as a novel tool for physical drying considered as a replacement of oven technologies^[3]. This opens new doors in high-energy consuming technologies to establish environmentally friendly technologies for applications in coating industry. These findings show the potential to design on demand tailor-made materials/absorbers.

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PHOTOSWITCHABLE ORGANIC NANOPARTICLES TOWARD BIOIMAGING

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Azo compounds have spread in the field of biology at a growing pace, especially for their photomechanical responses impacting considerably cell functions.¹ Most of them are employed as individual molecules, requiring high concentration or energy doses to activate enough molecules and obtain efficient responses. Following the interest paid to fluorescent organic nanoparticles in bioimaging for their high functional payload, we have developed self-assembled composite azo nanoparticles, rarely regarded.² Their capability as on/off indicators of drug model delivery has been harnessed to decipher the fate of nanocarriers after cellular endocytosis.³ We will also show how their photomechanical deformation can be addressed at the nanoscale level using combined AFM and *in situ* photoswitching, opening potentialities toward photoactivated cell destruction and enhanced photoacoustic bioimaging.

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Combining LED-driven photochemistry and Rose Bengal-anchored polymer colloids as an efficient strategy for carrying out photooxygenation process

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Organic photochemistry is a key synthetic pathway for sustainable chemistry.¹ In particular, photooxygenation reactions are very attractive:² (i) they involve only singlet oxygen, a powerful selective oxidant, produced by safe photosensitization of oxygen in the visible range at ambient temperature, and (ii) they are very efficient for preparing oxetanes, hydroperoxides and endoperoxides. Their industrial implementation is limited to a few examples in the flavour, fragrance or pharmaceutical industries, for which batch reactors equipped with energy-demanding mercury light sources are generally used.³ Continuous-flow microstructured technologies, combined with LEDs, are promising alternatives to batch photochemical processing.⁴ Most of the works considers a sensitizer solubilized in the reaction medium, while the concept of solid-supported sensitizers offers many advantages: (i) the separation of the sensitizer from the other products is then easier, and (ii) it is a strategy for transposing poorly soluble sensitizers into green solvents while simultaneously enhancing their photostability.

In this context, the present work studies the reactivity of poly(N-vinylcaprolactam-co-vinyl acetate-co-vinylbenzyl Rose Bengal) microgels as heterogeneous photosensitizers in a continuous-flow process. Photoactive colloids were synthesized by miniemulsion copolymerization of vinyl acetate, N-vinyl caprolactam, divinyl adipate crosslinker and vinyl benzyl Rose Bengal monomer.⁵

Experiments were carried out in a LED-driven spiral-shaped microreactor⁶ in which “slurry” Taylor flows were generated, allowing accurate control of irradiation (emission spectrum and intensity), light absorption (tunable absorbance) and gas-liquid flow conditions (volumetric and stoichiometric ratio). The benchmark photooxygenation of α -terpinene was implemented in ethanol to provide a green solvent using air as a safe supply of oxygen.

The swollen RB-grafted colloids in ethanol were demonstrated to be efficient in converting α -terpinene into ascaridole with high conversion and high selectivity, and in short residence times (few minutes).⁷ They exhibited a reactivity similar to that of the free RB, even with a lower quantum yield. Their photo-reactivity was stable over 8 months of storage with good reproducibility. Finally, they proved to be reusable during several cycles and to decrease the RB photobleaching levels compared to free RB.

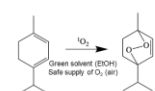
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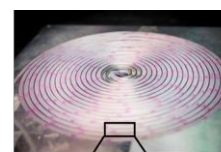
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LED-driven flow photochemistry



ROSE BENGAL-ANCHORED SWOLLEN POLYMER COLLOIDS



Air bubbles containing the reaction medium and the RB-grafted polymer colloids

Photo-generated diazonia for an anticancer therapy using light

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Recently, a photo-triggered intramolecular double nucleophilic aromatic substitution (S_NAr) has been discovered allowing the straightforward synthesis of the new compound **2** suitable for the development of an anti-cancer treatment. Indeed, diazonia **2** selectively stabilizes G-quadruplexes (G4) structures (Fig 1 left) and generates singlet oxygen.¹ In addition, thanks to the fluorescence of the photocyclized product **2**, its generation and localization may be followed up *in cellulo* (Fig 1 right).

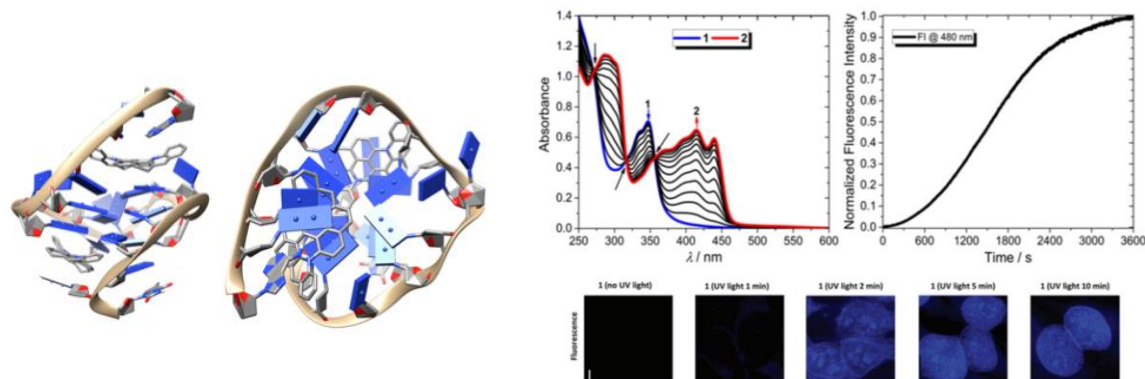


Figure 1 : Left : Representative structures of **2** in the presence of *c-MYC Pu22* G-quadruplex. Right : Photoconversion of compound **1** into diazonia **2** (in cuvette or *in cellulo*). Confocal fluorescence images of MeOH-fixed HeLa cells stained with **1** (10 μ M) upon UV irradiation.

Here, we have investigated the influence of the leaving group (Fig 2) on the photocyclization efficiency. The photoconversion quantum yield has been determined by UV-visible follow-up upon irradiation.² Therefore, we have designed a series of compounds **1** bearing a “non-innocent” leaving group linked to the aromatic core by the most efficient photolabile arms. Therefore, we are aiming at improving the pro-drug efficiency by choosing leaving groups bearing targeting groups or additional chemotherapeutic drugs inspired by photo pharmacology.³

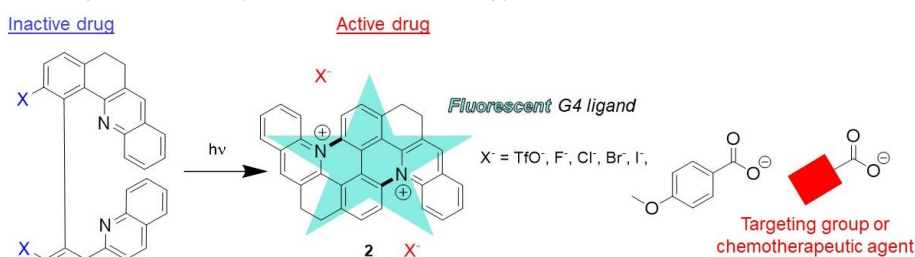


Figure 2 : Photoconversion of quinolizinium derivatives **1** into diazonia **2** for an anti-cancer treatment.

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Design and characterization of red-shifted photochromic molecules

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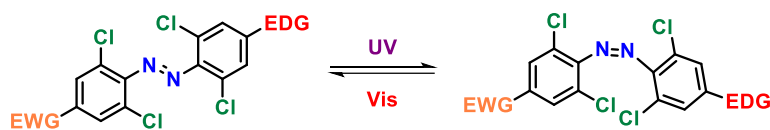
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Photochromic compounds are widely used to tune the properties of biomolecules or materials, using light as an external and non-invasive stimulus.¹ Especially, the organic photochromic materials are very interesting for potential photonic applications such as optical data storage and processing.²

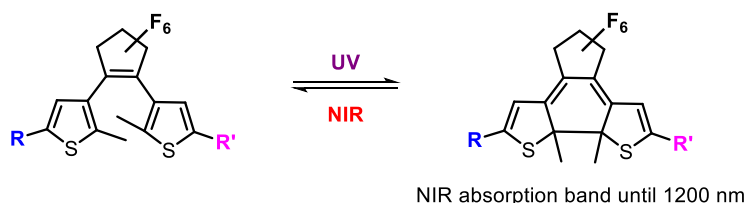
For such applications, we focused on (i) azobenzenes and (ii) diarylethenes photoswitches. Indeed, azobenzenes have proven to be efficient in processes such as molecular alignment or creation of relief grating. We synthesized new tetra-ortho-chlorinated push-pull azobenzenes (Scheme 1, i) and we studied the photochemical behaviour in solution and in polymer matrix. The photochemical properties are very promising, such as a red-shift band and very fast-relaxing photoswitching.

On the other hand, we targeted diarylethenes which are emblematic P-type photochromic molecules. We synthesized several π -conjugated diarylethenes (Scheme 1, ii) and we performed the photochemical characterization. These photochromic compounds disclose interesting properties, such as a near infrared (NIR) absorption band which is very attractive for the targeted applications.

(i) Synthesized push-pull **azobenzenes** : red-shifted and very fast-relaxing



(ii) Synthesized π -conjugated **diarylethenes** : red-shifted



Scheme 1: General structures of the targeted azobenzenes (i) and diarylethenes (ii)

Acknowledgements

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PROTON CRANES: WHAT THEY MEAN, HOW THEY OPERATE

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Proton cranes are single molecule systems, where a truly intramolecular proton transfer (IPT) takes place over a long distance under suitable irradiation [1-3]. They contain a mediator (side arm) connected to a tautomeric backbone through an axle and able reversibly to transport the proton between the proton-donor (PD) and proton-acceptor (PA) sites of the bistable tautomeric unit (Figure 1).

The overall process is based on a series of consecutive *switching steps* (a-c): excited state IPT (step a) leading to intermediate state(s), where the side arm rotates or not (step b) around the axle, depending on the relative strength of the competitive PA sites in the tautomeric unit. Finally, in a case of rotation, the proton, being derived on the other side of the tautomeric unit, is released to the local PA site through another IPT reaction (step c).

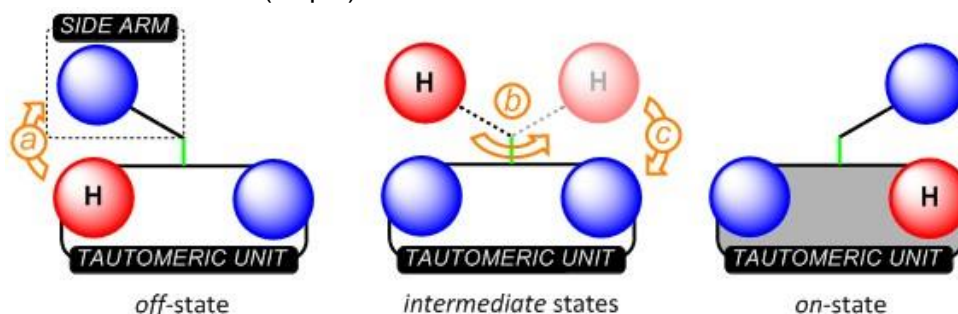


Figure 1: A sketch of the action of a molecular switch, operating through IPT mechanism. The PD sites are given in red, while the PA once are in blue.

In the current communication a variety of newly designed conjugated proton cranes, where the IPT leads to change in the character of the axle, will be considered [4-5]. The effect of the stator (7-OH quinoline or 4-OH coumarin) and the flexibility of the rotor (flexible or rigid) are the key parameters determining the mechanism of action and efficiency of switching.

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Structure-properties relationships in cyclic and linear fluorophores: two examples

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Small molecule fluorescent dyes found many applications in research, (bio)medicine and elsewhere. Their design is often based on a choice of chromophore moiety and substituents properties, electronic effects or just anecdotal evidence. Our investigations of several classes of such dyes brings new insights into the structure-properties relationships (SPR) in ring-embedded polymethines and xanthenes.

First, within a group of hemicroconaines **1** and croconaines **2**,¹ polymethines with embedded five-membered oxocarbon (larger analogue of squaraine), with various substituents we investigated spectroscopic properties, acid-base properties and established SPR. With help of NMR and quantum chemical calculations we also investigated their conformational behavior.

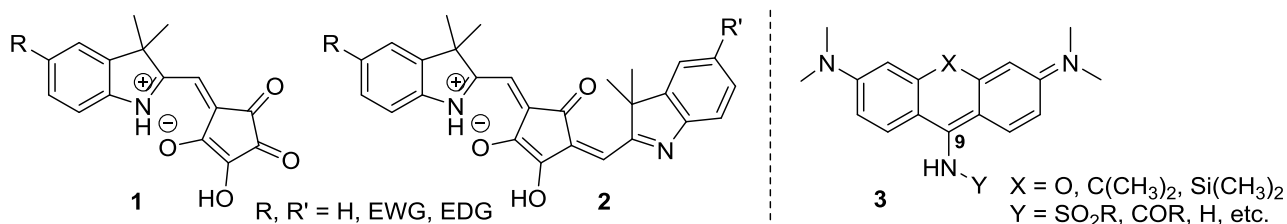


Figure : Croconaines **1**, hemicroconaines **2**, and 9-amino-pyrone **3** with various substitution patterns.

Second, we investigated a library of 9-amino-pyrone **3** and found that some exhibit bright fluorescence emission (Φ_f up to ~ 0.8), large Stokes shifts, and some are good pH indicators (with pK_a in neutral region).² Based on their spectroscopic properties and theoretical calculations, we build SPR and investigated steric effects impacts on excited state geometry and properties.

Details of both groups will be discussed from both experimental and theoretical point of view.

Acknowledgements

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Heterogeneous photoredox reactions and recyclability of an iridium(III) photocatalyst

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With new advances and a great deal of research being carried out in photocatalytic reactions, increasing attention is being devoted to this field. New synthetic routes can be achieved under mild conditions with excellent results, but the traditionally used photocatalysts are based on organometallic iridium(III) or ruthenium(II) complexes, with poor recoverability and reusability.¹ The increasing price of these metals has necessitated the exploration of heterogenization methods that facilitate their reuse in various catalytic cycles.

Our approach to this problem has been the synthesis of a new type of ionosilica, based on a cationic cyclometalated iridium(III) complex functionalized with triethoxysilane groups, which has been previously reported by our group (Figure 1).² This material has been used to study two different reactions, both under an oxidative quenching mechanism, and showing promising results in the recoverability of the material, making this heterogenization method a good alternative for transition metal-based photocatalysts.

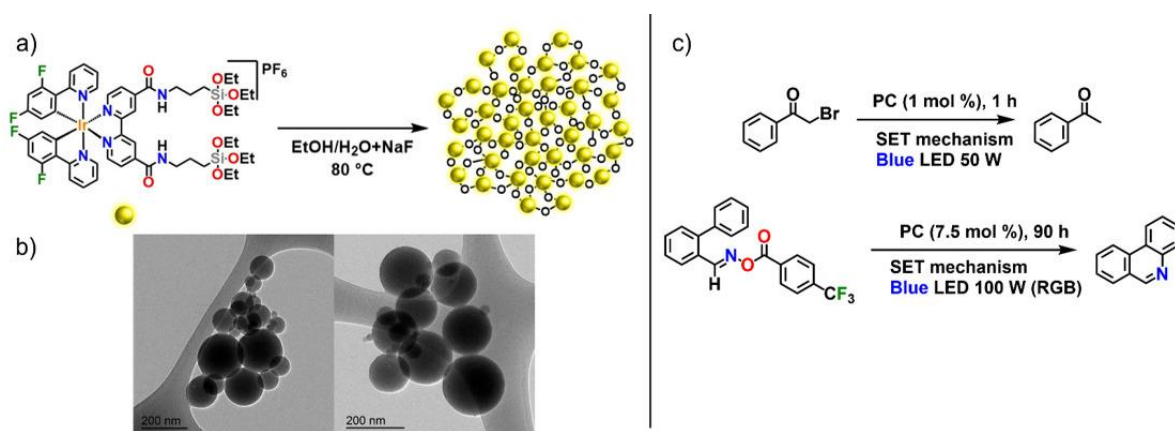


Figure 1: a) Iridium(III) complex and synthesis of the ionosilica; b) Representative TEM images of the material; c) Photocatalytic reactions studied.

Acknowledgments

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ULTRAFAST EXCITED STATE DYNAMICS OF THE ARCHAEORHODOPSIN 3 AND ITS MUTANTS

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Archaerhodopsin-3 (AR-3) is a light-driven proton pump found in *Halorubrum sodomense*. AR-3 was reported to display a detectable fluorescence, which, when integrated in membranes of live cells, was shown to depend strongly on the transmembrane voltage. AR-3 was then put forward as a possible candidate for optogenetic investigations, i.e. in the form of a *genetically encoded voltage indicator*¹ to track neuronal electric signals or for neural silencing. Also, multiple mutants then emerged², with fluorescence quantum yields (FQY) reaching up to 1.2% which is a 100-fold increase with respect to the wild-type protein (wt). 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 rhodopsins³. Other changes in terms of the electrostatic interactions of the protein cavity containing retinal chromophore are induced in the double mutant DETC and the quintuple mutant Arch-5². The fluorescence kinetics (figure 1) are measured with 200 fs time resolution using broadband up-conversion and transient absorption set-ups. 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 agree with the measured FQY's³. The excited-state lifetime increases for the different AR-3 mutants because of a potential barrier in the excited state induced by the interactions with the protein environment. Quantum chemical simulations⁴ predict the existence of such barrier, the height of which correlates, for different mutations, with the observed FQY. Unlike other retinal proteins, this barrier is predicted to arise from mixing of the ground and excited states. The influence of a possible mixture of all-trans and 13-cis isomers on the different excited state lifetimes is currently investigated by controlling the so-called light-adaptation conditions, which assure a dominant all-trans configuration.

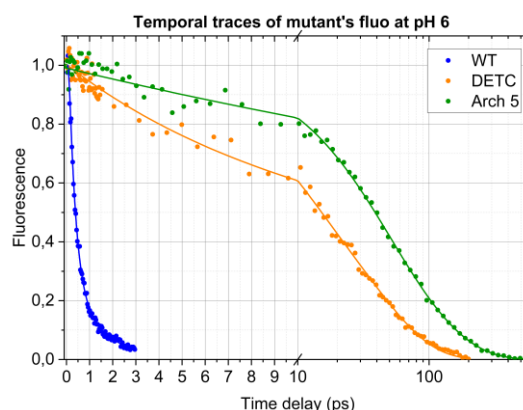


Figure 1: Fluorescence decays of AR-3, and the two mutants DETC and Arch-5, at pH6 on a semi-log scale

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Ultrafast spectroscopy of semi-transparent dye-sensitized solar cells

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Dye-sensitized solar cells (DSSCs) are newly emerging candidates for solar energy conversion applications. Our target is to utilize novel NIR organic dyes [1,2], advantageous for the implementation of semi-transparent devices designed for Building-integrated Photovoltaics. We investigated Pyrrolopyrrole-cyanine dyes (PPcys) [3], the absorption maximum of which is shifted in the near-IR part of the spectrum (> 700 nm). We report here combined Femtosecond Transient Absorption studies of a novel NIR absorbing dyes, named TB202 and TB207, in prototype devices based on operating TiO₂ electrode and of the non-productive high bandgap semiconductor (SC) Al₂O₃ electrode, as a reference.

Due to thienyl substitutions TB202 (see figure panel C) exhibits a strong redshifted absorption band peaking at 790 nm ($\epsilon > 100,000 \text{ M}^{-1}\text{cm}^{-1}$) and covering 650-800 nm when attached on SC nanoparticles. However, it has a lower power conversion efficiency (PCE) of 1.5 % as compared to the phenyl substituted TB207 based solar cell (PCE = 3.9 %) [4]. As reported previously, the main efficiency limitation in PCE is due to aggregate formation, inducing unwanted monomer-to-aggregate energy transfer (ET), which kinetically competes with the productive monomer-to-semiconductor charge transfer (CT) [4]. The VIS/near-IR ultrafast spectroscopy revealed the excited state absorptions (ESAs), which belong to the monomers, the aggregates and the monomer cation photoproduct, and the kinetic rates related CT and ET. The results show, that the charge transfer for TB202 is as slower than in TB207, and on the same timescale as ET.

In conclusion, with femtosecond VIS/NIR spectroscopy we have identified the origin of the different PCE of in TB202 and TB207 based solar cells. The thienyl substituted dye turns out to be limited by the small driving force for carrier injection.

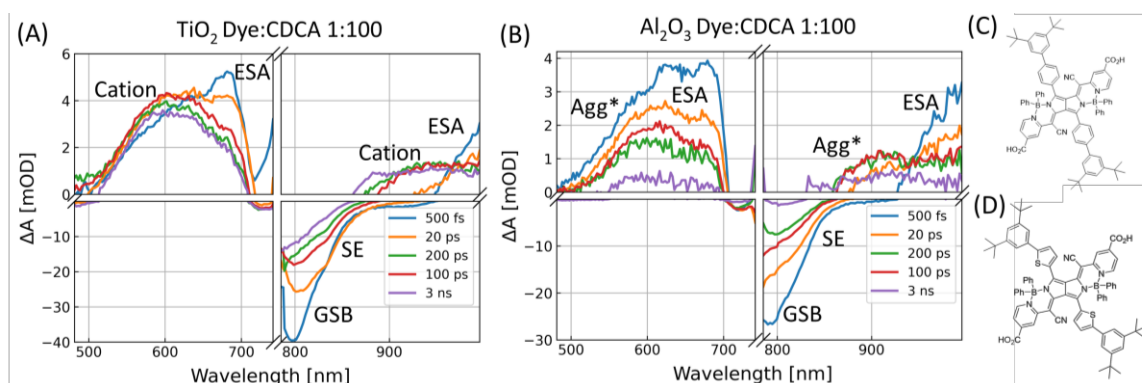


Figure: Transient absorption spectra of prototype cells based on TB202 mixed 1:100 with co-adsorbent CDCA on TiO₂ (B) and on Al₂O₃ anode (A) as a reference. The chemical structures of TB202 (C) and TB207 (D) are also displayed.

Acknowledgements

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Heteroleptic Copper(I) Complexes: Design Strategies, Excited State Properties and Photocatalytic Applications

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The development of novel and efficient photosensitizers based on earth-abundant metals is at the heart of our current research.^[1-6] In particular, we are focusing on heteroleptic diimine-diphosphine Cu^I complexes of the type [Cu(N[^]N)(P[^]P)]⁺.^[1-6] Driven by the goal of increasing the antenna system and improving the photophysical properties of these photosensitizers, the backbone of the diimine moiety has been extended using different strategies (see Figure 1). A general distinction is made between systems with directly fused acceptor units (left side)^[3,4] and covalently linked substituents at the 1,10-phenanthroline moiety (right).^[5,6]

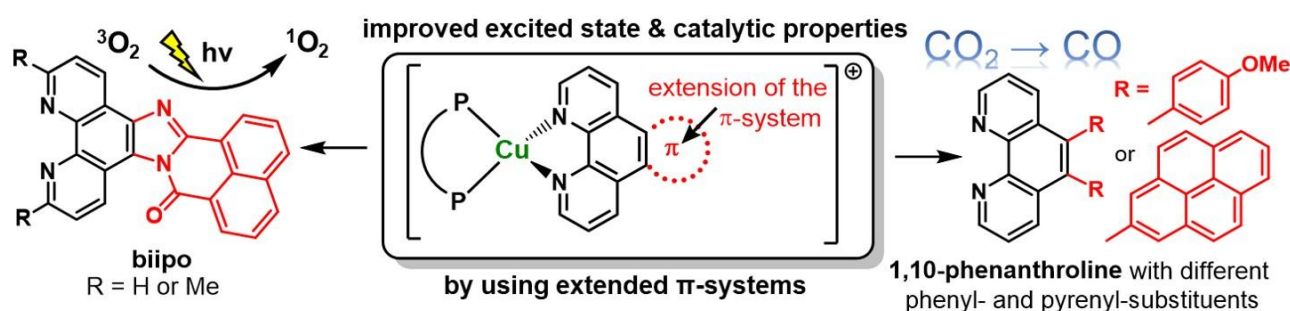


Figure 1: Representation of two different design strategies – The impact of directly fused (left) or covalently linked (right) extended π -systems on the photophysical and photocatalytic properties of the resulting Cu^I complexes.

This presentation illustrates the effect of different π -system extensions on the absorptivity, excited state lifetimes and electron storage capability of the resulting Cu^I photosensitizers. On the one hand, a new rylene-type diimine ligand (namely biipo) with a completely rigid and planar π -system in its backbone will be discussed (Figure 1 - left).^[3,4] On the other hand, several systematic series of selectively substituted 1,10-phenanthroline ligands containing either phenyl or pyrenyl substituents have been prepared (Figure 1 - right).^[5,6] In addition to the comprehensive spectroscopic characterization, these complexes were successfully applied in various photocatalytic reactions, e.g. the light-driven generation of reactive singlet oxygen (¹O₂), the activation of CO₂ and the reductive dehalogenation of aryl halides.

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Ultra-fast Energy transfer dynamics in dye-doped organic nanoparticles

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Photosynthetic organisms use Light Harvesting Complexes (LHCs), which are networks of interacting chromophores, to achieve optimum light energy absorption and conversion [1]. To mimic the function of LHCs, synthetic light-harvesting "antennas" are designed and applied to enhance the fluorescence emission of molecular probes in sensing and imaging applications [2]. In this study, we employ time-resolved fluorescence spectroscopy to investigate the photophysical properties of dye-doped, polymeric, organic nanoparticles (ONPs), which have been shown to exhibit a "giant" antenna effect [3].

This effect results from very efficient exciton diffusion within the nanoparticles. First, exciton energy transfer (EET) ensures efficient exciton migration within chromophores. To monitor the femtosecond timescale for exciton hopping to nearest neighbours, we use fluorescence up-conversion spectroscopy with polarization-resolved excitation and detection to measure time-resolved fluorescence anisotropy decay. We measure a temporal component of ≈ 300 fs and we observe an unresolved temporal component (<200 fs) highlighting an ultra-fast energy transfer. Furthermore, we found that the exciton population decay kinetics depend on the excitation fluence and reveal singlet-singlet exciton annihilation (SSA), a crucial parameter for determining the picosecond timescale for exciton diffusion within the ONP [4,5]. We also demonstrate the impact of the inhomogeneous intensity profile of the excitation beam on the apparent annihilation rate. We determine a high annihilation rate of $\gamma = 5 \times 10^{-9} \text{ cm}^3/\text{s}$ in the ONPs doped with 30w% of donors. These results underline a high efficiency of energy diffusion and transport within the nanoparticle which aligns with the high antenna effect mentioned above.

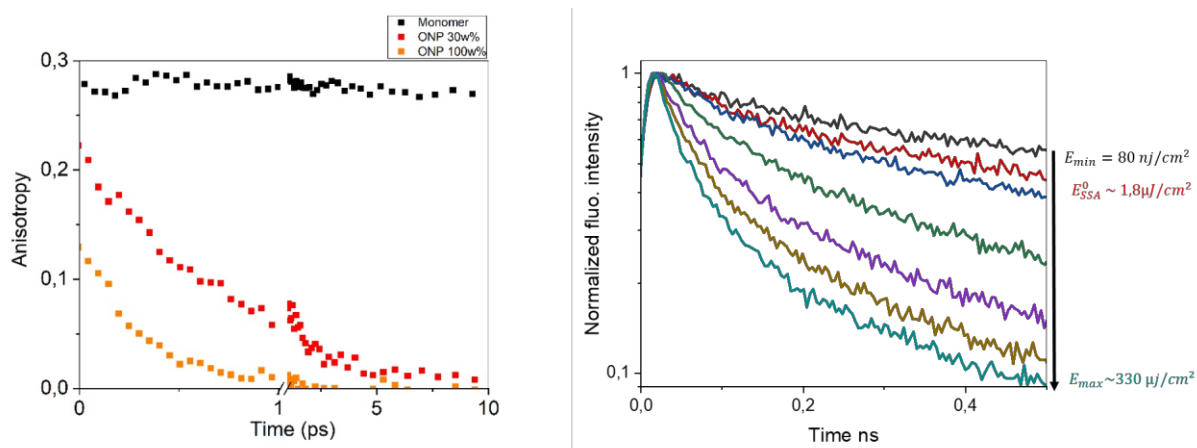


Figure: Exciton dynamics in ONPs. Left panel: Time-resolved fluorescence anisotropy measured using femtosecond up-conversion fluorescence spectroscopy for monomer rhodamine B, 30w% and 100w% dye-loaded ONP. The reduction of the initial anisotropy is the sign of a non-resolved (i.e. faster than 200 fs) EET process. Right panel: Fluence dependence of the population decay kinetics for 100w% dye-loaded ONPs. The arrow denotes the increasing fluence range used to excite the ONPs. The acceleration of the decay upon the increase of excitation reveals the SSA process.

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Photoinduced intramolecular electron and energy transfer in a photosensitizer-modified laccase

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Electron transfer (ET) reactions play a crucial role in various biological processes, such as photosynthesis. Understanding how electrons are transported in these complex systems can provide insights into developing novel tools to perform multielectronic chemical transformations. Notably, designing photocatalytic systems that exploit light energy to drive enzymes to perform both oxidation and reduction reactions is of significant interest.¹ The multicopper oxidase laccase couples the substrate's mono-electronic oxidation (at a T1 surface-located Cu²⁺ center) to the 4-electron reduction of O₂ into H₂O (at an embedded tri-nuclear Cu²⁺ center TNC) via successive intramolecular ETs. Here, a strategy is presented for achieving a controlled orientation of a ruthenium-polypyridyl photosensitizer graft on the surface of a fungal laccase. Laccase variants are engineered by site-directed mutagenesis with unique surface-accessible lysine residues (designated UNIKs) located at a desired position on the enzyme's surface. Ruthenium-polypyridyl-modified UNIKs are obtained by reductive alkylation of lysine residues,² allowing triggering and probing both fluorescence resonance energy transfer (FRET) and photoinduced ET processes from discrete surface grafting points relative to the redox-centers (both T1 and TNC). Olefin oxidation coupled with the reduction of O₂ occurs under continuous light irradiation. During the process, the Ru-UNIK hybrids undergo photoreduction, in which both the rate and extent of reduction are intrinsically dependent on the grafting location. In addition, under these experimental conditions, electrons can be directly injected into the TNC and subsequently transferred to the T1 center in a reverse intra-molecular ET process. The same effect is observed for O₂ reduction, the catalytic efficiency of each hybrid is improved under continuous irradiation depending on the grafting position. On the other hand, under laser flash irradiation – within the lifetime of Ru triplet metal-to-ligand charge-transfer excited state (³MLCT ~ 1 μs) – most of the interaction with laccase is dominated by FRET events that are dependent on the photosensitizer's position regarding the copper centers. Interestingly, the presence of laccase induces a higher-energy fluorescence state at 520 nm decaying according to the grafting position and with rate (τ₁ ≈ 5 ns) much faster than Ru ³MLCT. Furthermore, simulated Ru^{II}-Cu^{II} electron coupling values and distances allowed defining potential ET pathways throughout the protein matrix. In summary, the approach presented in this study provides valuable insights into intramolecular energy and electron transfer processes, as well as the repartition of electrons on the 4 Cu²⁺ ions. Our results showed that ruthenium-polypyridyl photosensitizers are amenable to deliver multiple electrons to buried active sites and sustain photocatalytic activity upon visible light excitation.

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Breaking the Resolution Limit in Two-Photon Microscopy Using Molecular Photoswitches

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Probes with two-photon absorption (2PA) property are commonly employed in fluorescence microscopy. The reason for 2PA use is the quadratic power dependence on the excitation probability with excitation light intensity, allowing spatially confined fluorescence. However, lateral and axial resolutions of 2PA microscopy is no better than 1PA confocal imaging. Theory foresees that by implementing 3PA or 4PA, substantial resolution gain can be obtained. Increasing the resolution by means of absorption processes with more than 2 photons is compromised because of the extreme excitation intensities required and non-optimal excitation wavelengths.

To circumvent these limitations, we developed a 2PA probe-photoswitch dyad to achieve comparable performance to 4PA. Entanglement of 2 two-photon induced processes via Förster resonance energy transfer (FRET) and photoisomerization in fluorene-dithienylethene derivatives allowed us to observe a near perfect 4-photon behavior. In a more recent study, we investigate the second generation of these dyads, based on photoswitches from other photochromic families.

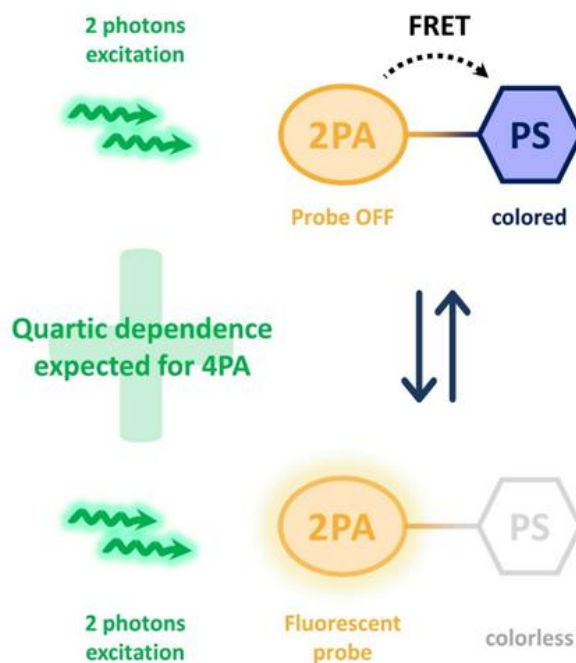


Figure: Two-photon absorbing probes-photoswitch (2PA-PS) dyads achieving 4PA performance

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Excited state energy landscape of phosphorescent group 14 complexes

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Transition metal complexes with emissive long-lived excited states are important for various photochemical and photophysical applications. A paradigm change has occurred in recent years, that the lighter first row transition metal complexes can show efficient intersystem crossing, populating long-lived excited states, with several applications.^[1] Yet, examples for photoactive/photoluminescent complexes of heavy main group complexes are rare,^[2] in particular for group 14 complexes in the oxidation state +II,^[3] the tetrylenes.^[4] Furthermore, the photophysical behavior and the nature of the phosphorescent excited states of these compounds have remained mostly unexplored.

Here, we present a new insight into the photophysical behavior of emissive tetrylene compounds based on two complexes E(bpep) (E = Sn, Pb H₂bpep = 2-[1,1-Bis(1*H*-pyrrol-2-yl)ethyl]pyridine). The present study shows that the tin(II) complex exhibits green intra-ligand charge transfer (³ILCT) phosphorescence, while the lead(II) complex only displays a weak red ligand-to-metal charge transfer (³LMCT) phosphorescence. The experimental results (UV/Vis-/steady state emission spectroscopy) and detailed (TD)-DFT calculations explain the observations and provide a new understanding for rational design principles for tetrylene complexes with long lived phosphorescence.^[5]

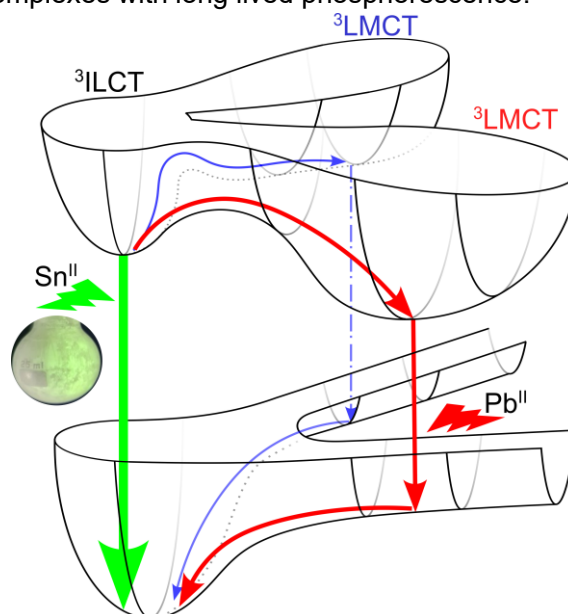


Figure: Schematic overview of the excited state energy landscape of the E(bpep) complexes.^[5]

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PANCHROMATIC ANTENNA INDUCED BY NANOGRAPHENE DECORATION IN NI-PORPHYRIN

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Femtosecond optical transient absorption spectroscopy and time-dependent density functional theory are employed to study, for the first time, photoexcited carrier relaxation in β -, meso-, β -triplyfused porphyrin-nanographene conjugate NPN (Figure 1). [1] This molecule exhibits an extended panchromaticity which arrives up to 1200 nm, with an onset of absorption matching the solar spectrum, making this compound a suitable candidate for high efficiency solar cells or photocatalytic processes.

Excited state dynamics reveal a primary singlet, delocalized along the molecule, that rapidly relaxes into a metal centered triplet, which acts as an antenna, to funnel excited carriers towards ligand-delocalized triplets. These results reveal porphyrin decoration with nanographenes is enabling a ligand-centered lowest triplet state formation of large spatial extension, an appealing performance in order to enhance interactions with electron scavengers. These results point towards novel design strategies for broadening the applicability of porphyrin-based dyes in optoelectronics.

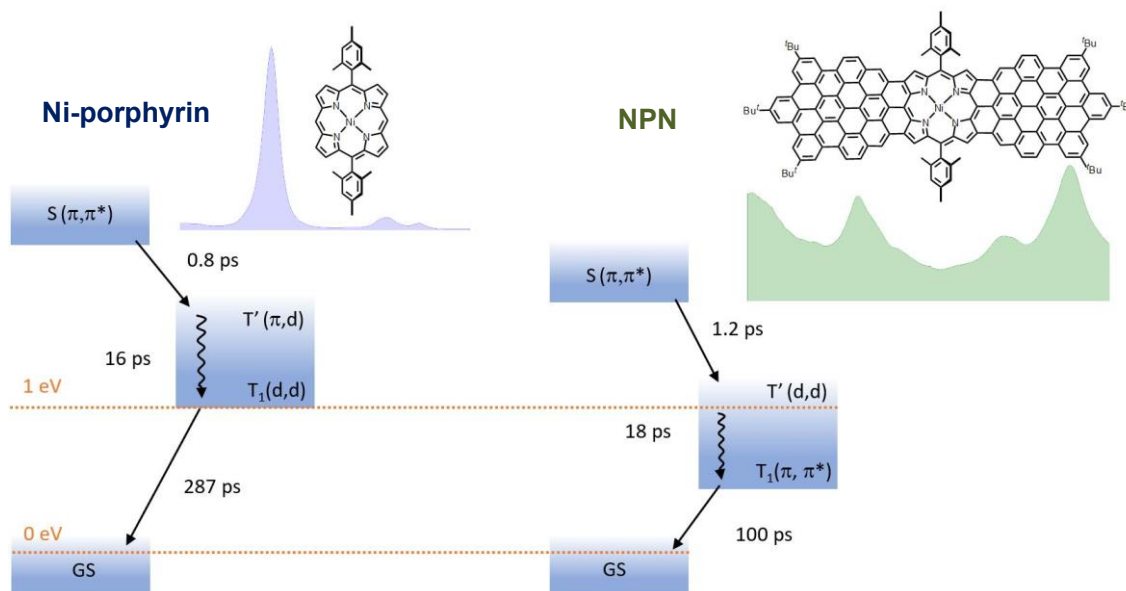


Figure 1: Photophysical scheme of deexcitation processes in Ni-porphyrin (right) and NPN molecule (left).

Constant rates are obtained by TAS measurements while energetic levels are obtained by TDDFT calculations.

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MULTI-STIMULI RESPONSIVE CHROMIC CYCLOMETALATED Pt(II) COMPLEXES

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Interest in chromic materials is rapidly increasing for their applications as smart responsive materials. The majority of the reported materials respond to one stimulus and few show multi-stimuli response. In this field, square-planar platinum(II) complexes have emerged as archetypal systems to understand the fundamentals of molecular self-assembly and related phenomena, including crystallization/polymorphism and aggregation-induced emission. Their rigid skeleton favor the formation of supramolecular structures through Pt \cdots Pt and/or $\pi\cdots\pi$ interactions and lead to unique photophysical properties, such as long-lived 3 MMLCT emission arising from metal–metal interaction of relevance in electronic devices, chemosensors or bioimaging¹. Particularly, cycloplatinated compounds containing strong field ligands are attractive platforms for self-assembled strongly emissive functional materials whose photophysical characteristics can be modulated by controlling their assembly, which constitutes a powerful tool for developing materials with stimuli-responsive luminescence properties.

In this context, one of our research projects concerns the self-assembly and photophysical properties of cyclometalated Pt(II) compounds with chloride/isocyanide, alkynyl/isocyanide and picolinate ligands of the form [Pt(C \wedge N)Cl(CNR)], [Pt(C \wedge N)(C \equiv CR')(CNR)] and [Pt(C \wedge N)(R-pic- κ -N,O)]. We demonstrate the fine modulation of molecular packing and emission properties by minor molecular structural variations or solvents using X-ray diffraction and theoretical studies²⁻⁴. They form aggregates through Pt \cdots Pt and/or $\pi\cdots\pi$ interactions in the ground and excited states, giving rise to different chromic behavior upon application of one or several stimuli.

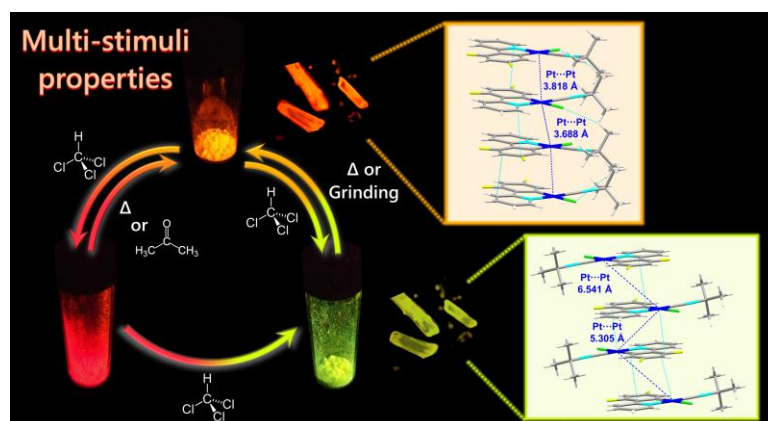


Figure: Multis-stimuli responsive properties and crystal packing of one of the complexes studied

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Unravelling the photoprotection mechanism of synthetic MAA analogues

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Sunlight is essential for living organisms, but it also presents some harmful effects. In humans, these damaging effects will be mainly due to the UV radiation. This portion of sunlight can induce permanent pigmentation and erythema which are potentially dangerous and can evolve into skin cancer. Therefore, the development of new photoprotection systems is an important issue mainly centered on industrial R&D.

In our research group we have designed a series of sunscreen molecules with improved capabilities inspired by natural Mycosporine-like aminoacids. These natural molecules are based on amino-cyclohexylimine core and exhibit high photostability, lack of fluorescence and strong UV absorption. However, their low availability and difficult extraction from marine algae have led to a new approach to obtain MAA-inspired molecules through organic synthesis in an affordable and scalable procedure.¹

During our synthetic approach, we reached two general families of compounds incorporating aryl and alkyl moieties in the imine residue. In our first studies both systems exhibit analogous photochemical properties beyond the small blueshift of alkyl derivatives. But investigation of both families revealed a more complex deactivation mechanism, moving from the naturally available out of plane deformation of alkyl synthetic derivatives, to a newly imine *E* to *Z* isomerization.²

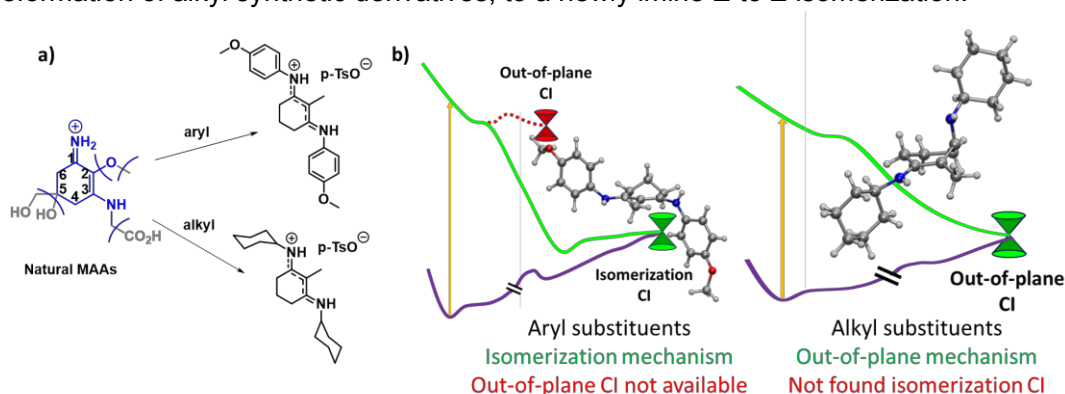


Figure 1: MAA inspired derivatives (a) and the proposed mechanism for light dissipation (b).

More recently we investigate these two mechanistic approaches by dynamic methods, aka time resolved spectroscopy and non-adiabatic molecular dynamics. In this work, we combine spectroscopy and molecular mechanics with the aim of finding experimental evidences and better understand how to improve the photoprotective ability in new families that we are synthesizing nowadays.

Acknowledgements

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How Do Phosphiranium Ylides React with Carboxylic Acids? Synthetic Scope and Mechanism.

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We present in this work the first phosphiranium ylide generation and discuss an unprecedented carbon-centred ring opening when combined with carboxylic acids (figure 1), thus by-passing the oxophilicity of phosphorus.¹

This methodology, using the photochemical generation of highly reactive electrophilic carbene, expands the scope of the reported difficult phosphirane quaternarization.^{2,3}

The peculiar properties of the previously unknown phosphiranium ylides are investigated and taken advantage of to lead to asymmetric phosphine oxides.

A reasonable reaction mechanism supported by DFT computational studies is then proposed.⁴

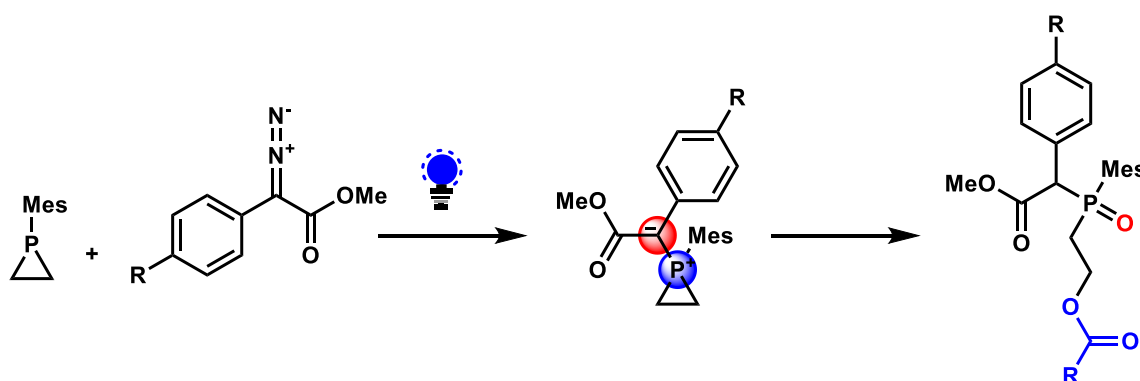


Figure 1: Phosphiranium ylide generation and subsequent ring opening. Mes = mesityl.

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Good Kobolds: heptacoordinate Co(II) catalysts for hydrogen evolution

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The most active cobalt-based catalysts for light-driven hydrogen evolution are usually based on hexacoordinate polypyridine complexes with a distorted octahedral structure.^{1, 2} We have challenged this paradigm by developing cobalt complexes based on a hexadentate polypyridyl ligand, which show an exotic heptacoordinate structure and outstanding performances with respect to their hexacoordinate counterparts.^{3, 4} In this talk the results of our investigations concerning the optimizations of such a class of catalysts are presented (Figure 1). In particular, the effect of the introduction of electron-donating and electron-withdrawing groups (aimed at haltering the ligand electronic properties) will be discussed and compared with the effect of the presence of groups potentially acting as proton relay units.^{5, 6} The impact of the variation of the electron transfer kinetic, deriving from the use of milder photochemically-generated reducing agents, will be also discussed.⁷ The aim of this talk is to provide an overview of the structure-activity investigation of this class of catalysts, providing new insights for the design of more efficient hydrogen evolution catalysts.

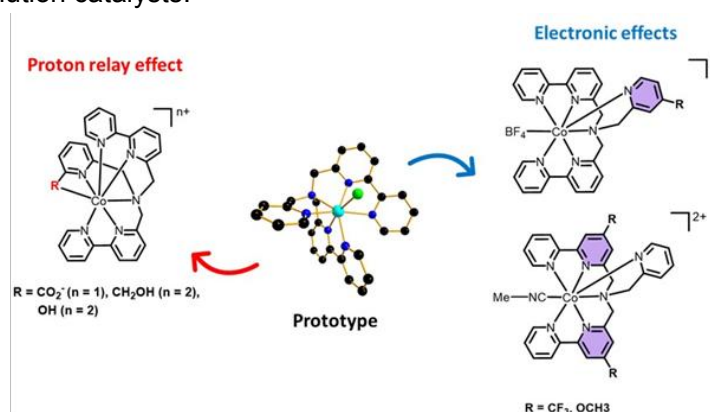


Figure 1: Families of heptacoordinate Co(II) complexes for efficient photochemical hydrogen evolution.

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Design of noble metal-free perylene photosensitizers and their integration in soft matter matrices for light driven hydrogen evolution

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Organic photoactive materials are promising candidates for molecular artificial photosynthetic systems because of their low cost, earth abundance, and the chemical tunability of their properties. Our work is focused on the design and synthesis of photostable organic photosensitizers like perylene monoimides that find application in photocatalytic water splitting. We will report on synthetic strategy we have developed for the preparation of photostable rylene monoimides that can sensitize $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters in aqueous solution for visible light driven hydrogen evolution and show remarkable influence of the substituents on the longevity of the longevity and nature of the excited state upon visible light excitation. Additionally, we will show how the incorporation of BODIPY or perylene photosensitizers in macromolecular templating agents as soft matter matrices can significantly improve the photocatalytic activity of photosensitizers and catalysts in light-driven hydrogen production.

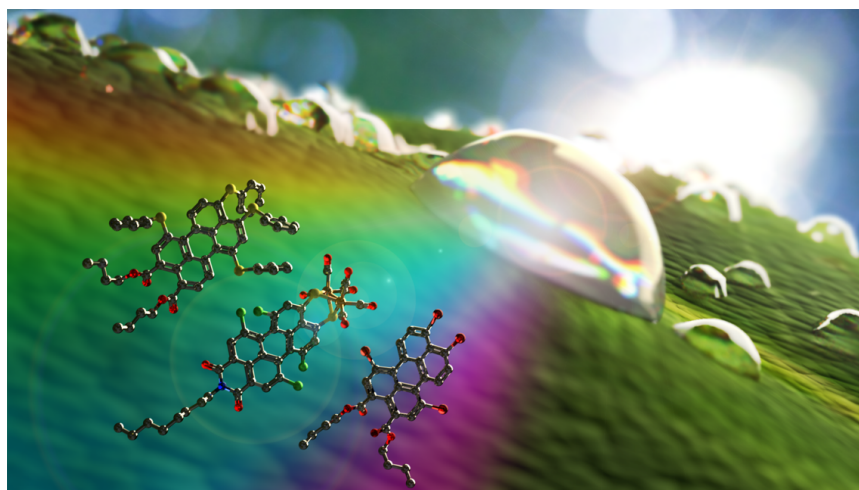


Figure 1. Graphic representation of perylene photosensitizers and the fine tuning of their properties by chemical modifications of the chromophore's scaffold

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Time-Resolved Spectroscopic Depiction of Photoinduced Electron Transfers in a Perfluorinated Zn-Porphyrin Sensitizer

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The daring promise of artificial photosynthesis to mitigate carbon dioxide (CO₂) emissions heavily relies on a vital comprehension of fundamental photoinduced charge transfer processes in carefully engineered biomimetic systems capable of charge separation^{1,2}. The light-absorbing unit in a prototypical photosystem, the photosensitizer, plays the fundamental role of kick starting the photoinduced dynamics of charge separation, sequential electron transfers and even electron accumulations on active catalysts capable of reducing CO₂. Although Ru-based photosensitizers remain unchallenged in terms of their photophysical properties, Zn-based tetraphenylporphyrin catalysts have been employed as possible alternatives in different applications³. In light of that, we set to study the reversible, light-induced dynamics of ZnTPP-F₂₀ in the presence of different electron donors and using time-resolved optical absorption and resonant Raman probes. Figure 1 presents the representations of the porphyrin and both electron donors used in this study – 1,4-diazabicyclo[2.2.2]octane (DABCO) and sodium ascorbate (NaAsc).

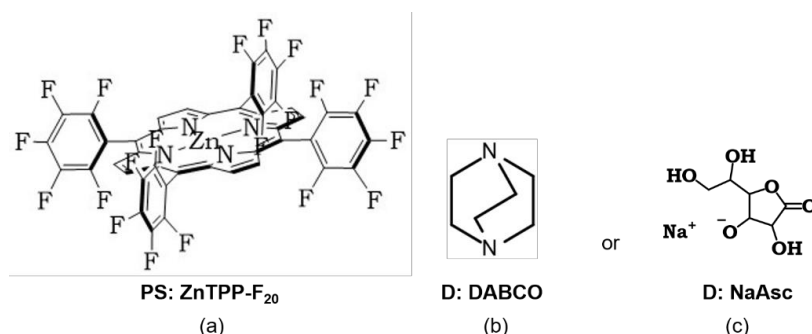


Figure 1. Representations of (a) ZnTPP-F₂₀, (b) DABCO and (c) NaAsc (PS = photosensitizer, D = electron donor)

In the presence of DABCO, due to its long-known ability to coordinate to the Zn center, the system behaves more like a dyad with much faster rates of formation and recombination of charge-separated states, in opposition to the case where NaAsc is used as a reversible electron donor in which the electron transfer kinetics is completely governed by diffusion. In this work, we show that time-resolved optical transient absorption and resonant Raman spectroscopies can be used as complementary approaches to study such charge separation reactions in a reversible manner.

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CO₂ Reduction in Organic/Water Mixtures with Heptacoordinated Polypyridine Complexes

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Fossil resources are receding while the global energy demand increases. Hence, the development of noble-metal-free catalysts capable of converting carbon dioxide into value-added compounds remains one of the central challenges in catalysis research [1]. Moreover, the possibility of catalyzing the CO₂ reduction reaction (CO₂RR) in water or organic/water mixtures currently represents an important target due to the possible competition with the hydrogen evolution reaction (HER). Recent efforts in the design of molecular catalysts for the CO₂RR have involved metal complexes exhibiting a high degree of electronic delocalization, which is useful in minimizing overpotential and maximizing selectivity over the competitive HER [2].

In this context, we report herein the comparison of the catalytic activity toward CO₂RR in water/acetonitrile mixtures of two molecular catalysts based on the redox non-innocent (1-([2,2'-bipyridin]-6-yl)-N-([2,2'-bipyridin]-6-ylmethyl)-N-(pyridin-2-ylmethyl)-methanamine) ligand [3], only differing for the central metal ion, as represented in Fig. 1a. In particular, a cobalt(II) and an iron(II) complexes have been prepared and characterized, both showing an exotic heptacoordinated structural motif. Their catalytic activity towards the CO₂RR in water/organic mixtures has been examined under both electrochemical and photochemical conditions using [Ru(bpy)₃]²⁺ as the sensitizer and N,N-diisopropylethylamine (DPEA) as the electron donor, as shown schematically in Fig. 1b. We anticipate that, in spite of the apparent structural similarity, completely different catalytic behaviors have been found, highlighting how simple metal replacement can induce remarkable changes in the catalysis of the CO₂RR.

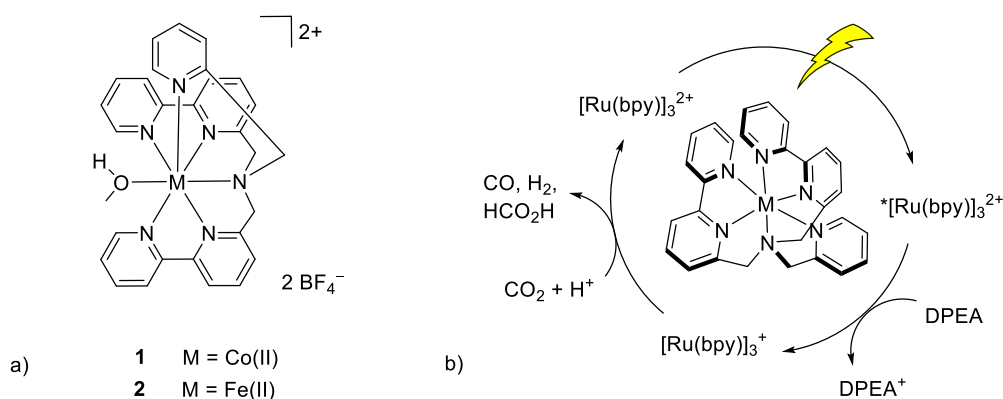


Figure 1 a) Molecular structure of complexes 1 and 2 used in the present work and b) schematic representation of the photochemical CO₂ reduction system

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PHOTOCYCLOADDITIONS WITH LIGNIN DERIVED AROMATIC COMPOUNDS

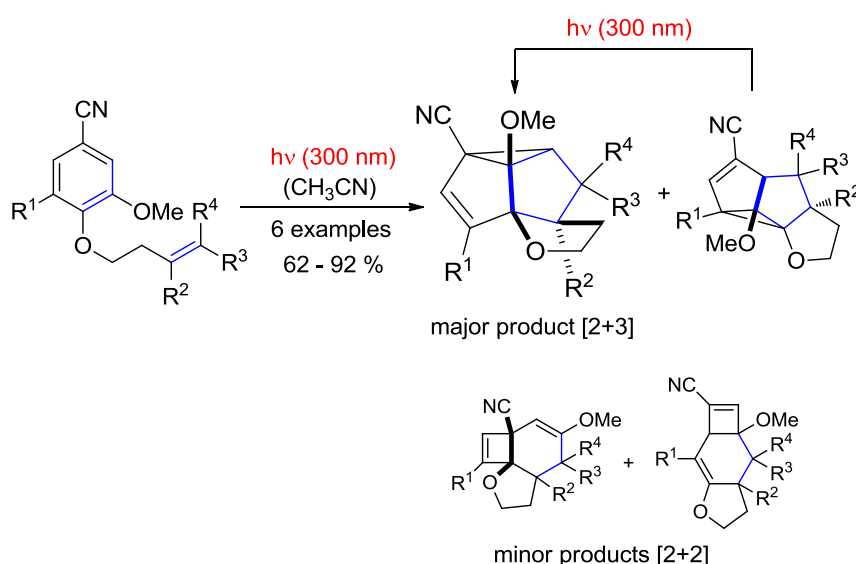
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Starting from simple compounds, photochemical reactions such as photocycloadditions of aromatic compounds with alkenes give access to products with a high degree of molecular complexity and diversity in only one step. [1] Three cycloaddition modes have been reported: (1) [2+2] or ortho photocycloaddition and consecutive reactions, (2) [2+3] or meta photocycloaddition and (3) [2+4] or para photocycloaddition. Often, these reaction modes are in competition with each other. In this context, we became interested in such reactions with aromatics derived from lignin and more particularly from vanillin. [2]

We investigated intramolecular photocycloaddition reactions of benzene derivatives possessing electron acceptor and electron donor substituents as they are derived from vanillin (Scheme). [3] These functional groups and their position as well as the spin multiplicity of the excited state have a significant impact on the competition between the different cycloaddition modes.



Scheme : Intramolecular photocycloadditions of aromatic compounds.

Acknowledgements

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SOME INTERESTING FEATURES OF PHOTOREDUCTION KINETICS OF BENZOPHENONE

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The characterization of the light-induced reactions of benzophenone (**Bp**) with alcohols served as the basis of modern molecular photochemistry. However, there are still numerous unanswered questions about the details of the mechanism. Triplet **Bp** participates in numerous reactions even in acetonitrile, a solvent considered as inert, such as phosphorescence, intersystem crossing to the ground state, photoreduction by the solvent, self-quenching with ground-state **Bp**, and triplet-triplet annihilation. Although these processes are all mentioned in the literature, the rates and nature of the reactions are not well understood. We present our newly obtained experimental kinetics results and their relationship with the thermodynamic parameters calculated from the modified Weller equation.

In our earlier work,¹ combined experimental and theoretical studies of the photoreduction kinetics of various substituted **Bp** derivatives with 2-propanol showed that two hydrogen bond complexation processes play a crucial role in the rate of the secondary hydrogen transfer step, ($RR'COH + Ph_2CO \rightarrow RR'CO + Ph_2COH$), influencing the product distribution. Depending on the substituent of **Bp**, large differences were observed in the rate coefficients of both in primary (${}^3Ph_2CO + RR'COH \rightarrow Ph_2COH + RR'COH$) and the secondary photoreduction, caused by the change in activation energy. Extending the kinetics studies, all relevant reaction rate coefficients were determined for the photoinitiated reactions of 3Bp with aliphatic alcohols (methanol, ethanol and 2-propanol) in neat alcohols and in two inert solvents. The rate constants of both reduction steps show huge differences depending on the nature of the alcohol and the solvent. Although the rate constant of both reduction steps decreases in the 2-propanol \rightarrow methanol direction, in the primary step the increase of the activation energy is responsible for the change of the rate constant, whereas in the secondary reduction, the decrease of the preexponential factor is reflected in the rate constant reduction. The possible mechanism will be discussed in detail.

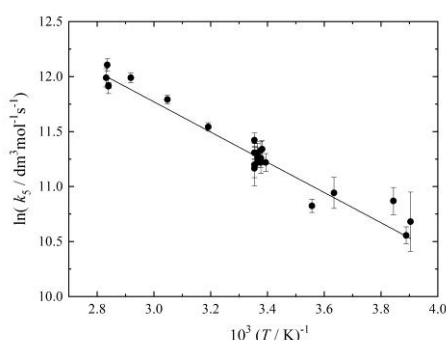


Figure : Arrhenius plot of the rate coefficient of the secondary hydrogen transfer reaction (k_s) measured in ethanol.

Acknowledgement. Thank for the National Research Development and Innovation Office of Hungary for the financial support [grant number OTKA K-128395].

References

FROM MOLECULAR ENGINEERING TO 3D FUNCTIONAL MATERIALS FOR METAL CATIONS DETECTION

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Keywords: Luminescence, sensing, photo-induced electron transfer, 3D material

The shift from uniform bulk materials to engineered micro-sized 3D functional organic and polymeric based materials is prone to bring unprecedented opportunities with regard to imaging, information storage or sensing.^{1–3} In the latter case, a particular challenge concerns the ability to manage the surface functionalization of the materials and provide versatile approaches toward micro-sized multi-analytes sensors.⁴

In this context, we propose an unprecedented design of 3-in-1 molecular modules, combining probe and photo-clickable units together upstream to the grafting step on the surface of 3D-polyacrylate materials.

We will focus on the design of supramolecular modules which are composed of three parts, ① a two photon active tetrazole core leading to the formation of pyrazolines upon a photo-induced cycloaddition to the surface acrylate functions, ② a pro-fluorescent pyrazoline-Bodipy pair; ③ a recognition unit. These modules provide the essential functions for our purpose: *i*) grafting by photo-induced cycloaddition (NITEC)^{5,6} at the surface of polyacrylate materials figure Step i) via one- or two-photon activation; *ii*) formation of pro-fluorescent species supported on the surface: the pyrazoline-Bodipy pairs whose fluorescence is quenched by photo-induced electron transfer (PET ON); *iii*) detection of metal cations by complexation to specific receptors, by means of fluorescence restitution (PET OFF).^{7–10}

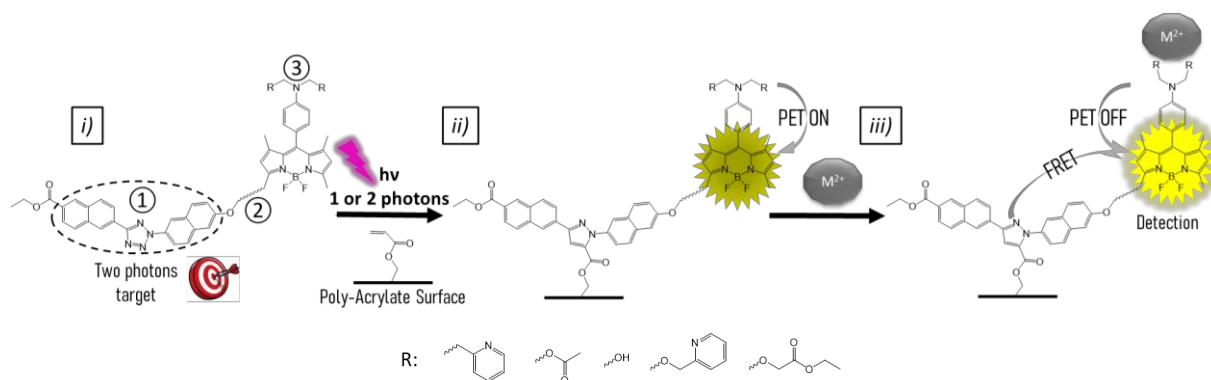


Figure 1: ① Two photons target tetrazole part, ② Pro-fluorescent pyrazoline-Bodipy pair, ③ Recognition unit

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LOW-ENERGY CONSUMING INITIATING SYSTEM BASED ON A SYNERGISTIC APPROACH FOR THE POLYMERIZATION OF ELIUM® THERMOPLASTIC RESINS

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Following a general awareness about the environmental issues and in order to respond to the climate emergency, the extensive use of thermoset composites intends to be replaced by the use of recyclable materials¹. As a result, a new configuration of Metal Acetylacetonate Bidentate Ligand Interaction (MABLI) mechanism adapted to the chemistry of the recyclable Elium® thermoplastic resins has been recently discovered to initiate the free radical polymerization under mild conditions². This initiating strategy is based on the synergy between the initial MABLI couple and a phosphine oxide (Type I photoinitiator). Despite the absence of irradiation, the mere presence of the phosphine oxide reduced significantly the curing time. To dismantle the role of each component and to predict new high-performance MABLI redox initiating systems based on a similar configuration, a mechanistic study was pursued. It has resulted in the identification of new hybrid complexes obtained by ligand exchange between the photoinitiator and the metallic complex. On the other hand, the presence of the Type I photoinitiator can level up the initiating strategy by combining MABLI and photoactivation into a dual cure approach.

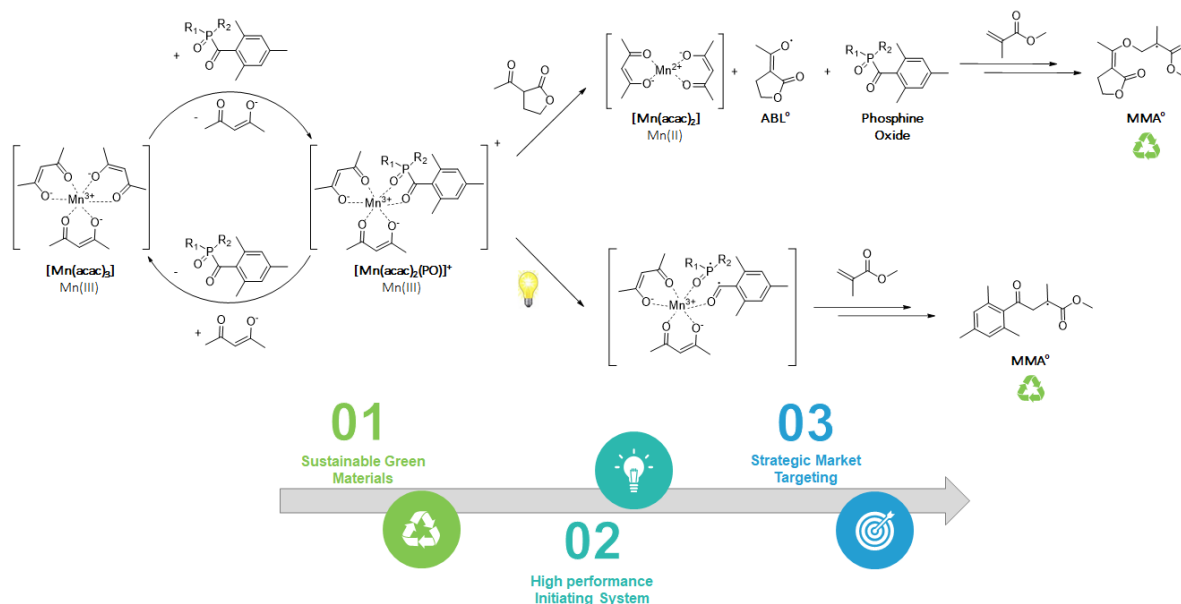


Figure 1: Proposed chemical mechanisms for the FRP initiation using the three-component initiating system

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INFLUENCE EXTERNAL VOLTAGE ON EXCITED STATE DYNAMICS OF 8'-APO- β -CAROTENAL.

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The intramolecular charge-transfer (ICT) state is a typical excited state for carbonyl carotenoids that contain a carbonyl group in their conjugation. It becomes pronounced only in the polar environment and is strongly coupled to the S_1 state, forming a new electronic state, usually denoted S_1 / ICT. If present, it leads to decreases in the S_1 lifetime compared to nonpolar environments. For example, the S_1 state of carotenoid 8'-apo- β -carotenal, as synthetic models of carbonyl carotenoids, has a lifetime of 25 ps in non-polar solvent n-hexane, but is reduced to 8 ps in polar solvents such as methanol or acetonitrile. However, the influence of applied voltage on ICT has not yet been investigated. Therefore, this work examines the influence of applied external voltage on the excited-state properties of 8'-apo- β -carotenal in acetonitrile by steady-state and ultrafast time-resolved absorption spectroscopy. Steady-state absorption spectra were recorded under applied voltage conditions to examine the S_2 state energy. Time-resolved absorption spectroelectrochemistry to study the excited state dynamics of 8'-apo- β -carotenal in acetonitrile to reveal the effect of applied voltage on the ICT state. The data collected as a function of the applied external voltage were compared with the data from standard measurements. The steady-state measurements showed that although the intensities of the S_0 - S_2 absorption bands vary significantly with applied voltage, their spectral positions remain nearly constant. On the basis of analysis of the transient absorption spectra under applied voltage, the voltage-dependent behaviours were observed. Comparison with standard pump-probe measurement shows that the magnitude of the ICT-like band decreases during the experiment under applied voltage condition, also associated with a prolongation of the S_1 /ICT-like lifetime from 8 ps to 13 ps. Furthermore, cutting off the applied voltage resulted in returning to no-voltage data within about 30 min. We have obtained satisfactory results demonstrating that the ICT state of carotenoids is possible to tune by applying an external voltage.

JOINT EXPERIMENTAL AND THEORETICAL INVESTIGATION OF EXCITED STATE VIBRATIONAL COHERENCES IN Mn SINGLE MOLECULE MAGNETS

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Single molecule magnets (SMM) are typically large poly-metallic molecules with two degenerate magnetic ground states that retain magnetisation under a so-called "blocking temperature". In d-metal molecules, the blocking temperature is very low, rendering most industrial applications impossible. The lowest blocking temperature is observed in the Mn₁₂ complex that retains magnetisation for months below 2K¹. Magnetic recording using femtosecond laser pulses has recently been achieved in some dielectric media, showing potential for ultrafast data storage applications. Light control of magnetisation represents a great challenge in the field of data storage as it opens the way for larger and more compact storage arrays. Yet, SMMs remain largely unexplored using ultrafast techniques.

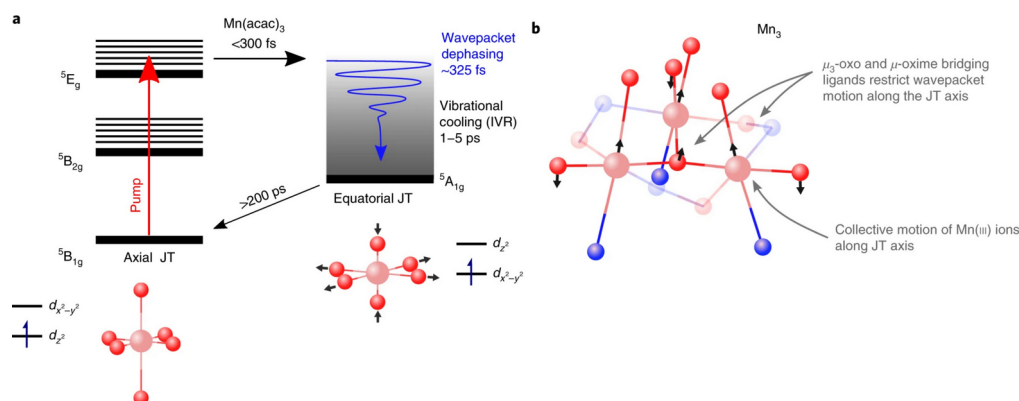


Figure : (a) Proposed relaxation pathway after excitation at 400nm. (b) Representation of the vibrational mode responsible for the observed coherences.

In this work^{2,3}, we investigate the photophysics and excited-state relaxation of a series of Mn(III) SMM, whose magnetic anisotropy is closely related to the Jahn–Teller distortion. Ultrafast transient absorption spectroscopy in solution reveals oscillations superimposed on the decay traces due to a vibrational wavepacket (WP). A joint experimental and theoretical study on Mn monomers allows to shine light on the origin of the vibrational coherences observed experimentally on the larger Mn₃ complex. It is shown to emanate from the μ₃-oxo-bridge effectively constraining the WP motions along the Jahn-Teller axis. Our results provide new possibilities for optical control of the magnetisation in SMMs and open up new molecular-design challenges to control the WP behaviour in the excited state of SMMs.

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Exploring Anti-Kasha Fluorescence in Azulene Derivatives for Proton Sensing Applications

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Kasha's rule dictates that an organic fluorescent molecule will only fluoresce from its lowest excited singlet state irrespective of the excitation energy. As a result, the wavelengths of photoluminescence and the fluorescence lifetime are independent of the excitation energy. Despite the broad applicability of Kasha's rule to various molecular systems, certain organic molecules can contravene this principle. An example of such a departure is the conspicuous observation of anti-Kasha fluorescence emanating from the S_2 energy level in azulene. Building on the anti-Kasha emission property of azulene molecules, we have designed and synthesized a novel derivative, 4-(azulen-2-yl)-N, N-dimethylaniline, and performed absorption and emission spectroscopy in various solvents, such as dichloromethane and ethanol. Further exploration of this molecule involved protonating it at different concentrations of trifluoroacetic acid (TFA) to investigate the photochemical and photophysical characteristics of its protonated structure. Time-dependent density functional theory (TD-DFT) and the second-order algebraic-diagrammatic construction methods (ADC(2)) have been utilized to model the absorption and emission properties of the investigated molecules and their protonated structures. [2] We compared the calculated results with the experimental data, which enabled us to effectively explain the absorption and emission spectra obtained from the experiment. Furthermore, through vibronic calculations we were able to successfully model the fine structure of the absorption and emission spectra. The computational results and experimental spectra of the neutral molecule without protonation demonstrate a strong S_2 emission peak, indicating its anti-Kasha emission property. The emission spectra obtained from the monoprotinated and diprotinated structures of the molecule proved to be originated from the S_1 state. This suggests that the azulene moiety of the molecule becomes more electronegative upon protonation, leading to a smaller energy gap between the S_2 and S_1 states and an increased rate of internal conversion, thereby restoring Kasha's emission. Given this characteristic, 4-(azulen-2-yl)-N, N-dimethylaniline can be further designed and applied as a proton sensor in analytical or biological imaging environments.

Acknowledgments

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Pas de Deux of a nitrosyl Couple: Synchronous Photoswitching from a Double-Linear to a Double-Bent in a metal dinitrosyl photoinduced linkage isomer

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Reversible molecular photoswitches are of great interest in the search for fast and sensitive materials that can be used for building photonic devices or molecular machines [1]. In this context, photoinduced linkage isomerism (PLI) in transition-metal nitrosyl compounds is of importance since the reversible photoswitching of the NO ligand is accompanied by significant photochromic and photorefractive changes [2]. In order to better understand the PLI mechanism responsible for these exciting properties, the knowledge of the bonding and activation of NO is essential. Here, we present for the very first time {Ru(NO)₂}¹⁰ dinitrosylruthenium complex [Ru(NO)₂(PPh₃)₂] showing photo-induced linkage isomerism (PLI) of a special kind (Figure 1): the two NO ligands switch, on photo-excitation, *synchronously* from the ground state (GS) with two almost linear RuNO functions to a metastable state (MS) which persists up to 230 K and can be populated to ≈ 50% [3]. The MS was experimentally characterised by photo-crystallography, IR spectroscopy and DS-calorimetry as a double-bent variant of the double-linear GS. The experimental results are confirmed by computation revealing the GS/MS transition as a disrotatory *synchronous* 50° turn of the two nitrosyl ligands. Only the synchronous disrotatory motion of the pair of nitrosyl ligands, pictorially the *pas de deux* of a nitrosyl couple, allows a smooth transition free of too many bond ruptures. As a result, there is an activation barrier that makes both isomers tangible. This type of motion might find application in molecular motors, since low doses of yellow light can switch it on, inducing a movement in one direction.

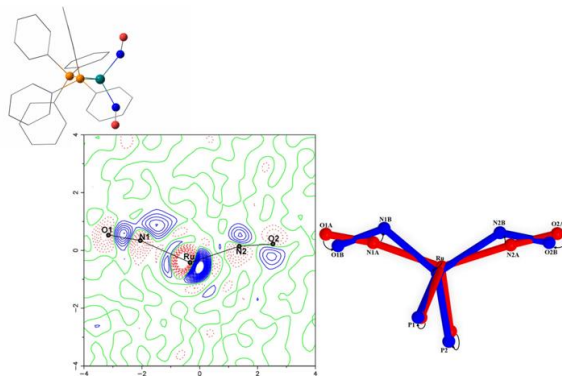


Figure 1. Left: Photodifference map after irradiation with 590 nm laser at 100 K; blue: positive values, red: negative values; contour-lines every 0.5 e Å⁻³. Right: comparison of GS and MS structure illustrating the (I-NO-κN)² GS to the metastable (a-NO-κN)² MS configurational change.

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P60	Zizzi	Federico	PHOTOSWITCHABLE NANOPARTICLES AS POTENTIAL HIGH-CONTRAST PHOTOACOUSTIC AGENTS

Light-driven H₂ evolution by [Mo₃S₁₃]²⁻ and an amphiphilic ruthenium-photosensitizer in biomimetic phospholipid bilayers

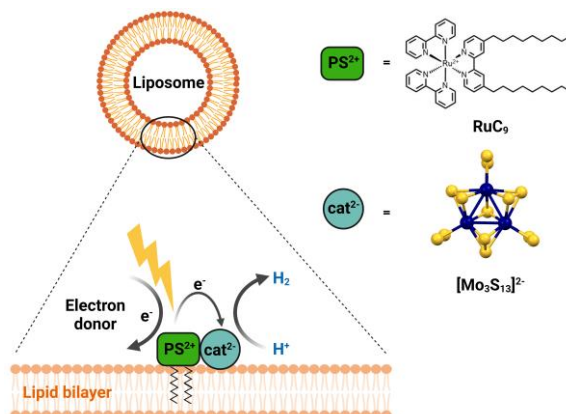
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The transition to a sustainable energy economy requires the development of technology to exploit abundant and renewable resources that can be used to generate green fuels such as hydrogen gas (H₂). One of the most promising process is the light-driven splitting of water by artificial photosynthesis using bioinspired systems.¹⁻² Here, we report the model of an artificial photosynthetic system for light-driven hydrogen (H₂) evolution. The system is based on liposomes where an amphiphilic ruthenium trisbipyridine based photosensitizer³ (RuC₉) and the H₂ evolving catalyst [Mo₃S₁₃]²⁻, a well-known HER catalyst active in organic solvent,⁴ are embedded in biomimetic phospholipid membranes. Although all tested lipid matrixes, including DMPC, DOPG, DPPC and DOPG liposomes provided similar liposomal structures, only DMPC yielded high H₂ amounts. When using DMPC as the main lipid the catalytic activity ($TON_{cat} \sim 200$) increased compared to purely aqueous conditions. Structural liposome properties are characterized by dynamic light scattering and transmission electron microscopy (TEM) analysis, while light-driven H₂ generation is carried out in a 3D printed open-source photoreactor.⁵ Quantification of H₂ was done and characterized by gas chromatography. The mechanism of excited state charge transfer is revealed by steady state and time resolved emission spectroscopy.

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

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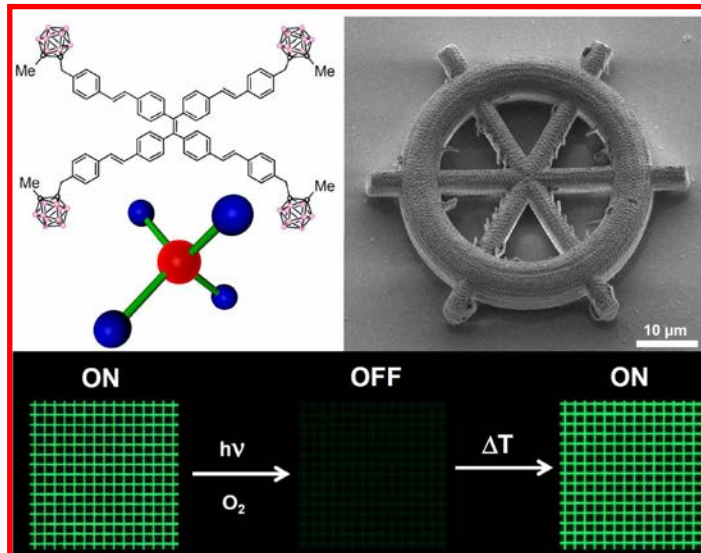
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Keywords: Two-Photon Absorption, 3D-Stereolithography, Stimuli Responsive Photomaterials

Two-photon polymerization (2PP) has emerged as one of the most efficient maskless stereolithography[1]. Such a direct laser writing method allows the fabrication of intricate 3D-structures with a spatial resolution down to the sub- μm scale. The unique capability of 2PP relies on its diffraction unlimited spatial confinement due to the non-linear absorption of the initiator component which is photoactivated at the focus point of a tightly focalized *fs*-pulse laser[2]. 2PP technology which is now commercially available

has been largely dedicated to the photopatterning of advanced functional materials with plethora applications such as photonic metamaterials[3], stimuli responsive devices[4], microelectromechanical systems or micromedicine[5, 6]. In this context, the two-photon initiator clearly has a pivotal role and should both exhibit significant two-photon absorption (2PA) cross-sections as well as an efficient quantum yield for the generation of reactive species that promote monomers cross-linking. With this respect, we present herein a



series of o-carborane-based derivatives with quadrupolar or octupolar geometries with significant two-photon activation ability. Such a non linear absorption property has been oriented for 2PP fabrications of emissive microstructures whose fluorescent can be alternatively 'switched off' and 'switched on' through light and thermal stimuli. This strategy proposes thereby a two-photon patternable materials for reversible data storage applications.

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Design and Synthesis of novel dinuclear Cu(I) complexes as TADF emitting materials

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Metal-organic complexes showing thermally activated delayed fluorescence are of particular interest, as they combine a theoretically internal quantum yield of 100% at moderate temperatures with economically friendly materials such as copper. These compounds can be used as emitting materials in OLEDs^[1], for instance, but also as photoinitiators in 3D experiments^[2].

In our group, various copper(I)-complexes using different monodentate ancillary phosphine ligands as well as *N,P*-bridging ligands based on 2-diphenylphosphinopyridine were developed and synthesized.^[3] Thus, a large class of luminescent Cu(I) complexes bearing a butterfly-shaped Cu₂X₂ core (X = halides) was obtained (Figure 1). Based on this, we are developing related species and compare the influence of the ligand binding site on the emission wavelengths. Hence, novel neutral mono-, di- and tetranuclear Cu(I)-complexes are synthesized and analyzed regarding their crystal structure via X-ray diffraction. To increase the solubility in common organic solvents functionalized groups are introduced into the ligands. The research is supported by computational calculations and photophysical characterization carried out by collaboration partners, as well as the execution of 3D experiments to test the photoinitiating properties of the complexes.

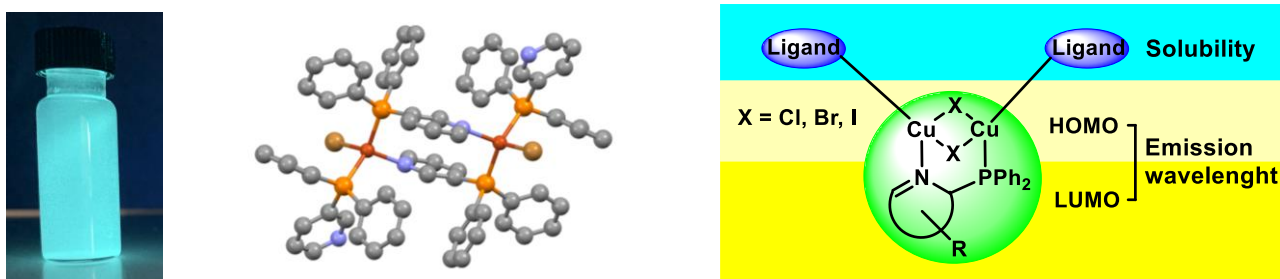


Figure 1: Left: Luminescence of an obtained complex under UV-light. Middle: Crystal structure of obtained complex. Right: Depiction of the general design strategy.

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Development of composite photoresists for 3D and 4D printing

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The association of elements with 3D/4D printing to manufacture new composites is leading to an increase in the number of applications related to various fields such as robotics, medicine, pollution control, etc. The design of this type of material in 3D printing is still rare and does not result in high quality objects. In this communication, we introduce a simple route to fabricate composite materials exhibiting dual stimuli. Special attention has been paid to the design of 4D composite in order to bring a fine control to the reversible shape deformation. One of the key parameters lies in the insertion of metallic gold nanoparticles into hydrogel object to confer it a 4D feature. In a first step, a description of the synthesis of the nanoparticles followed by the analysis of the morphology/size/dispersion by UV-vis spectrum and TEM imaging is performed. Several mixtures were prepared by varying the concentration of nanoparticles, with the aim of observing its impact on the photoreactivity/viscosity of the formulations and their printability. Resolution and fidelity criteria regarding the CAD model were assessed by investigating printed objects by SEM microscopy. Finally, camera tracking combined with different mathematical models are used to understand the swelling and thermal properties of these objects. By playing with the light intensity or the nanoparticles concentration, the increase of temperature can be controlled in a precise manner leading to the production of a 3D object that responds to a dual stimuli: moisture for swelling and heat for returning the printed object to its initial size. By taking advantage of the synergy between these dual properties, progress to various fields such as soft robotics can be envisioned.

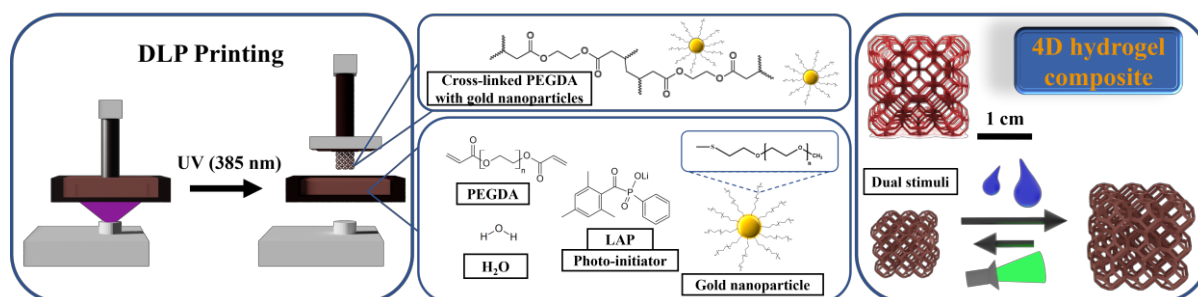


Figure : Global outline of the subject.

Acknowledgements

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When click chemistry modulates the photophysics

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Fluorescence is paramount for numerous applications in a wide variety of fields. Thus, the development of new class of fluorescent dyes with improved photophysical properties has been an important research field in the last decades. The use of new dyes for different purposes generally requires of their incorporation into larger structures. However, this often imposes a major synthetic challenge.

In light of this, we have devised new fluorene-based push-pull fluorophores inspired by a previous work.¹ The innovative synthetic approach minimizes the number of synthetic steps and allows readily implementation into larger scaffolds *via* click chemistry. More interestingly, the resulting triazole moiety affects to the overall photophysical properties, as it increases the electron-withdrawing character of the neighbouring carbonyl group. This effect is responsible for the stabilization of the LUMO and translates into red-shifted absorption and emission with respect to the parent compounds. This is a surplus to the already excellent photophysical properties of this class of dyes, including enhanced fluorosolvatochromism and large two-photon absorption cross sections. Theoretical studies support the experimental results as well as constitute the basis for designing new potential derivatives.

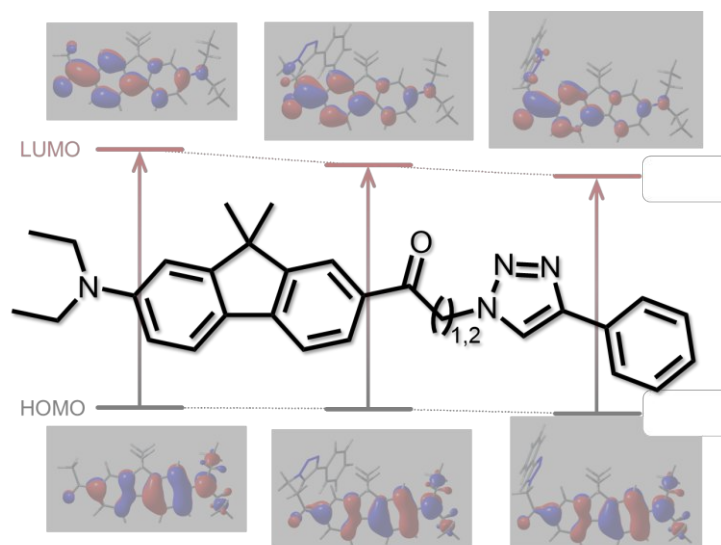


Figure: General structure and frontier molecular orbitals of the compounds devised.

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Synthesis and characterization of azobenzene glycoconjugates, towards the elaboration of chiroptical azo-glycophanes with multistate switching

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Azobenzene-based glycoconjugates (ABGs) are a class of photochromic carbohydrate derivatives that were first used in the early 2000s to probe carbohydrate-protein interactions.¹ Owing to the photochemical *E/Z* isomerization of the azobenzene switch, the physico-chemical and biological properties of ABGs may be altered with light, opening new horizons in many domains, especially glycosciences.² Lately, the azobenzene moiety was embedded in carbohydrate-based macrocycles, resulting in photoresponsive glycophanes with unique properties.³ Notably, these compounds demonstrated intriguing chiroptical switching, due to a chirality transfer from the carbohydrates to the photoswitch, a restricted conformational freedom and light-controlled water-solubility. In continuation of this research, a methodological investigation allowed the development of new synthetic pathways towards azo-based linear and cyclic glycoconjugates.⁴ A highly efficient palladium-catalyzed thioarylation of halogenated azo-derivatives with glycosyl thiols allowed the generation of ABGs, which photochromic properties could be modulated *via* oxidation of the bridging sulfur atoms. Importantly, one-pot procedures were developed for the heterogeneous bis-functionalization of azobenzenes. Finally, this reaction was used in the synthesis of macrocyclic glycoazobenzene dyads incorporating two different chromophores, which demonstrated multistate switching (Figure). Very interestingly, one of these macrocyclic dyads could be selectively switched in the four possible isomeric states with light only. Such derivatives may be of great interest in many applications, and we believe that their unprecedented switching properties might draw a lot of attention.

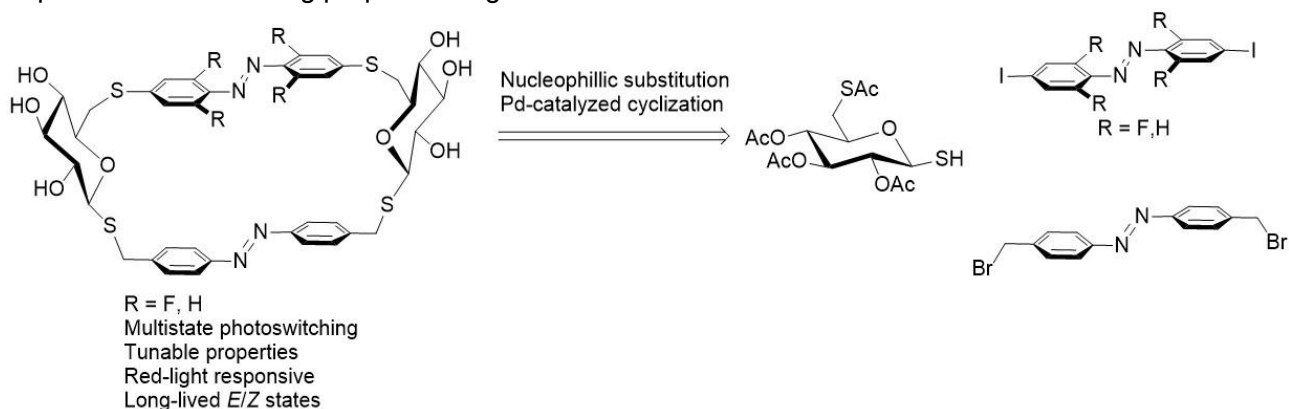


Figure: Retrosynthetic strategy of the formation of macrocyclic glycoazobenzene dyads

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Energy transfer in phospholipid bilayers for an oxidative conversion in liposomes

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In natural photosynthesis, light absorption and energy conversion takes place in different subunits which are spatially confined by the integration into the thylakoid membrane. In the light harvesting complex I and II are various chromophores to absorb light of different wavelengths and channel the photon's energy transfer to the reaction center.^[1,2] One mechanism for harvesting light at various wavelengths is Förster resonance energy transfer (FRET). FRET is a dipole-dipole interaction in which a photo-excited donor transfers energy to a distant ground-state energy acceptor at up to a range of around 10 nm.^[3,4] FRET was investigated between a selected donor-acceptor pair within the lipid bilayers of vesicles (Fig.1). It was previously shown that compartmentalization of a model substrate by liposomes/vesicles accelerates its light-driven oxidation by photochemically generated ¹O₂.^[5]

In the here presented work, it will be shown how the use of a light-harvesting FRET pair can lead to synergistic effects in light-driven oxidation of NADH as model substrate within liposomes.

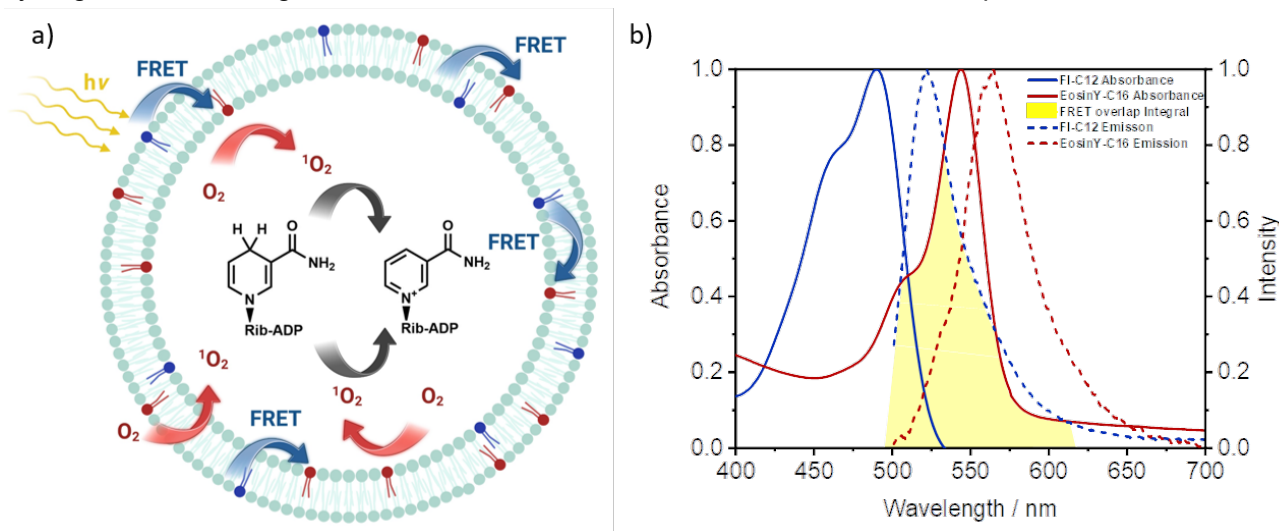


Figure 1: a) FRET in a phospholipid bilayer and production of NAD⁺ via ¹O₂, b) Spectral overlap of FI-C12 and EosinY-C16

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NEW PHOSPHINE OXIDES PHOTOINITIATORS FOR 3D PRINTINGL.BUCHON^{1,2,*}, J.M. BECHT^{1,2}, J. LALEVEE^{1,2}¹ Université de Haute-Alsace, IS2M, UMR 7361, CNRS, Mulhouse, France² Université de Strasbourg, IC, UMR 7361, CNRS, Strasbourg, FranceEmail: loic.buchon@uha.fr

3D printing is the technology of choice for the rapid production of objects with complex morphologies and controlled physical and chemical properties [1]. 3D printing by photopolymerization is of great interest because of its ability to access very small scales and its high resolution. In the case of recent 3D printers, the preferred wavelength for irradiation is 405 nm since it is a safe and energy-economical irradiation [2]. For 3D printing to be effective, it is therefore necessary to develop easily accessible, stable and highly efficient photoinitiating systems at the 405 nm wavelength. Furthermore, with the increasing use of photoinitiators, it is essential to develop new compounds with low cytotoxicity [3]. Hence, the development of new photoinitiators is currently of major interest.

In this work, the physical properties (triplet energy, bond dissociation energy, cleavage reaction enthalpy, absorption properties) of numerous molecules have been calculated by molecular modeling and the most promising compounds have been synthesized. Four phosphine oxides photoinitiators have been prepared in only two steps and characterized. Subsequently, their absorption properties were measured and their efficiencies in photopolymerization under LED irradiation at 405 nm were evaluated. Among the obtained photoinitiators, two of them showed a better efficiency than BAPO in photopolymerization ($R_p/[M_0] \times 100$ for CPO-2 = 6.94 s⁻¹, $R_p/[M_0] \times 100$ for ADPO-1 = 12.95 s⁻¹ and $R_p/[M_0] \times 100$ for BAPO = 4.93 s⁻¹) and one of the synthesized photoinitiators was successfully used in 3D printing (CPO-1). Finally, one of the synthesized photoinitiators (ADPO-1, Fig 1) showed a lower cytotoxicity than the benchmark compound TPO.

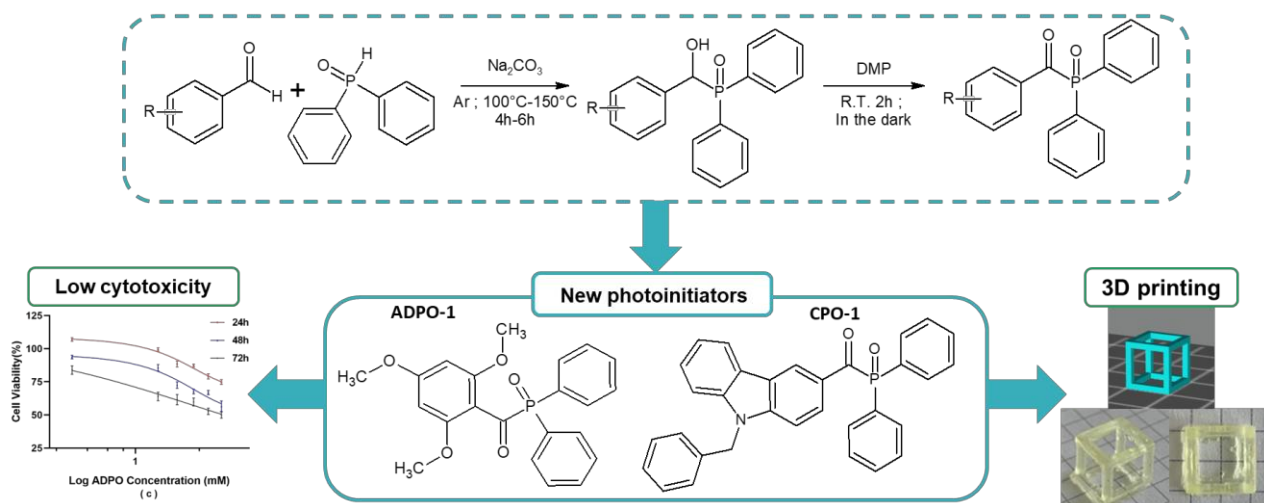


Figure 1: Synthesis of new photoinitiator, 3D printed object and cytotoxicity with the new photoinitiator

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Multi-activatable photochromic system: pH-dependent properties of diarylethene derivatives

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Photochromic molecules can undergo reversible isomerization by light irradiation, switching from an A form to a B form, which have different physical and chemical properties.¹ The back reaction can occur either by light irradiation (P-type photochromism) or spontaneously (T-type photochromism).

In our work, we target systems on which pH can activate the back reaction, changing from a neutral P-type form to a protonated T-type form.² We studied two diarylethene derivatives substituted with pyridine moieties.³ The pKa values of the open and the closed forms could be measured by spectroscopic titration and their photochromic properties were investigated by steady-state spectroscopy and photokinetic experiments, supported by DFT and TD-DFT calculations. Both molecules exhibit a thermal stability in a neutral environment and a spontaneous back return in an acidic environment, due to the protonation of the pyridine moieties.

Hence, these molecules demonstrate the possibility to trigger the B→A back-reaction “on-demand” and to modulate its kinetics varying the acid concentration (Figure 1a). They can act as multi-activatable system with the ability of changing from a P-type to a T-type photochromism by chemical stimulus (Figure 1b).

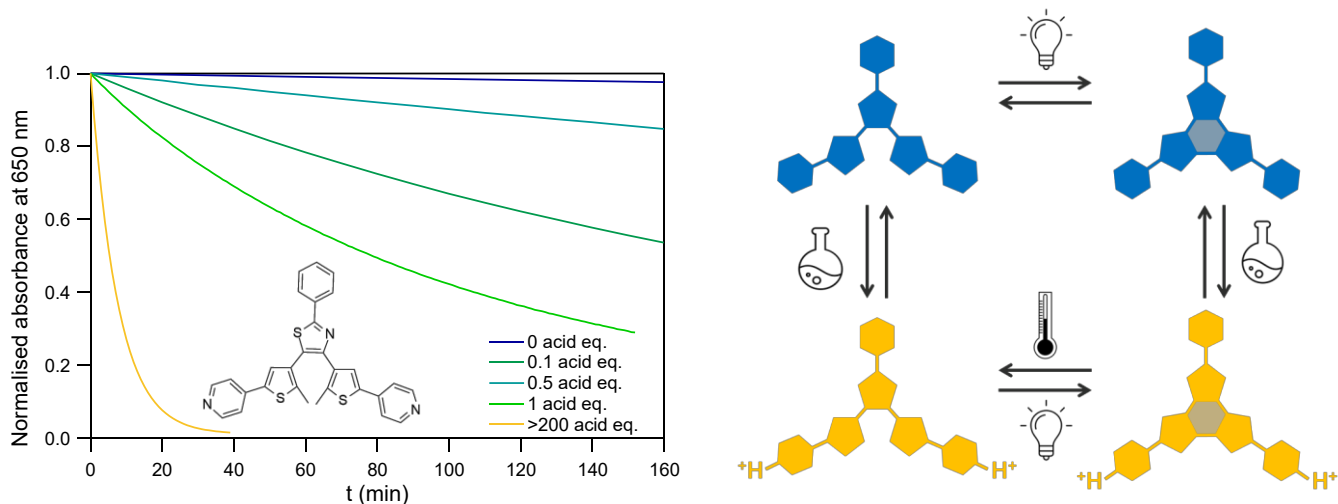


Figure 1. a. Kinetics modulation of the back reaction b. Schematic representation of the multiactivatable system

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Photochemical Valorisation of Lignin

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Lignin is a potential feedstock for bio-based chemicals production. However, its recalcitrance and heterogeneity have limited its use so far. Light can be used to convert lignin into small and valuable chemicals at mild temperatures and pressure. Up to date, most work has focused on heterogeneous and homogeneous photocatalysis. Although such methods showed encouraging results, the synthesis, separation, and recycling of catalysts would add significant costs to the process. Therefore, our work is mostly focused on the photolysis of lignin without the addition of photocatalysts.

We have used UV light (265 and 280 nm) to depolymerize lignin in a variety of solvents.¹ The observed changes in functional groups and molecular weight distribution indicated depolymerization of lignin. More recently we investigated the effects of benzophenone as a photosensitizer to depolymerize lignin (Figure 1).² We found that benzophenone sensitization has different effects on Kraft lignin and the model compound 2-benzyloxyphenol. Our further studies are within understanding the photophysics of lignin to apply that knowledge on developing scalable light induced routes to depolymerize different types of lignin.

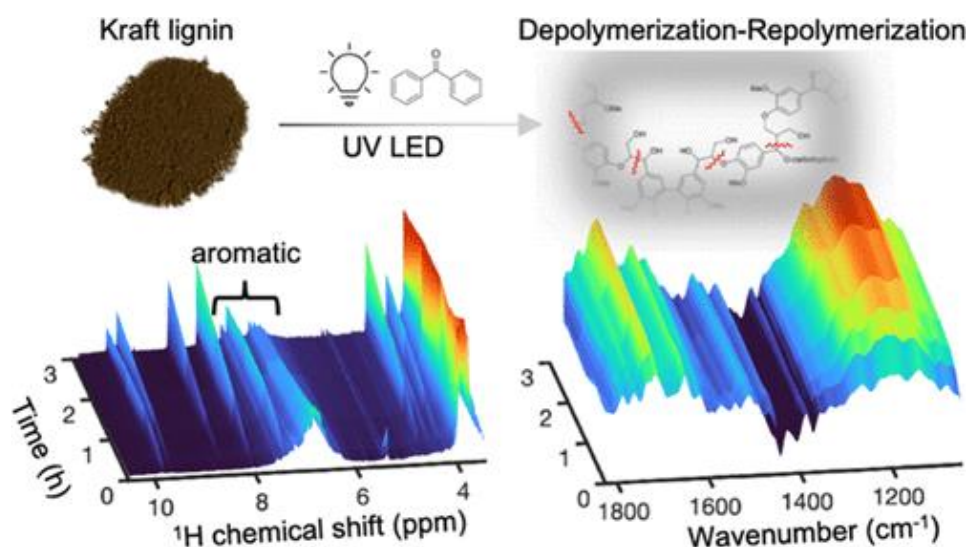


Figure 1. NMR and FTIR are used to monitor changes in functional groups and bonding of lignin samples over irradiation time.

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Remote Electrostatic Repulsion Triggered by Excited State Antiaromaticity Relief as Origin of Photoacidity

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Photoacids are compounds turned more acidic under photoirradiation, and they can be used to promote organic synthesis.¹ We found that the newly synthesized compound **HDMAPAN-(BF₄)₂** shows an exceptionally low computed pK_a^{hv} in the S₁ state (-12.3), 14 units below the ground state pK_a . Interestingly, the photoexcitation affects the acidity of the anilinium proton, despite the S₀ → S₁ electronic transition is located in the dibenzotropylium unit. Our computational results using TD-DFT suggest that the photoacid is functioning by a new mechanism: upon photoexcitation, the positive charge within the flanking rings in the dibenzotropylium unit is localized on the carbons closest to the anilinium ring, creating an increased electrostatic repulsion against the acidic proton (Figure 1).

Furthermore, computed ΔpK_a , ($\Delta pK_a = pK_a - pK_a^{hv}$) was gradually reduced as insulating spacers between the anilinium and dibenzotropylium units were added, while the approach of a fractional positive charge destabilizes the anilinium unit. Both experiments supported our hypothesis of photoacidity mechanism. Finally, we identified the excited state antiaromatic character of the dibenzotropylium unit in the S₁ state as the possible cause to the local reorganization of charge distribution to alleviate the destabilizing excited state antiaromatic character.²

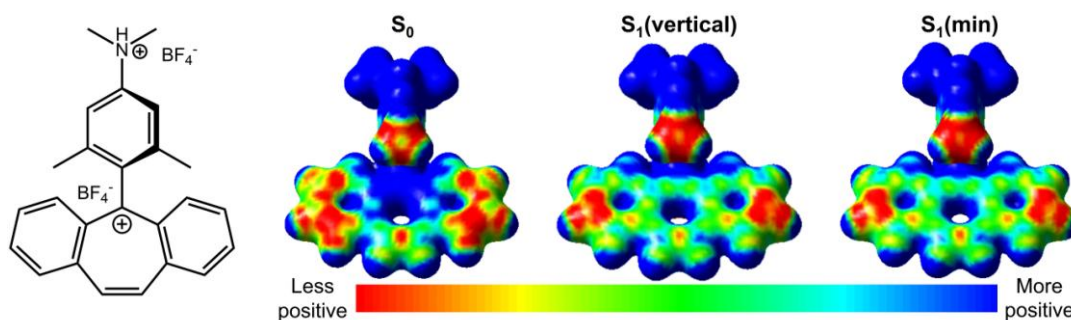


Figure 1: Structure of the photoacid **HDMAPAN-(BF₄)₂** and its electrostatic potential maps computed at different electronic states. Calculated at CAM-B3LYP-D3/6-311+G(d,p) level, solvent = water.

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PHOSPHORESCENT CYCLOMETALATED Ir(III) COMPLEXES WITH ACETYLIDE AND ISOCYANIDE LIGANDS

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Over the last years, numerous studies have been carried out on d^6 phosphors, such as Ru^{II} or Ir^{III} and d^8 Pt^{II} compounds, due to their potential application in different optoelectronic fields. In particular, cyclometalated Ir(III) complexes display very high photophysical performances due their good photostability, high photoluminescent quantum yields (Φ_{PL}), facile color tunability and long-lived triplet excited states. Furthermore, this class of complexes has been applied to a variety of photonic applications including oxygen sensing, biological labeling, photosensitization, and emissive materials in organic light emitting diodes (OLEDs)¹. These complexes usually display mixed metal-to-ligand charge transfer/ $^3MLCT/^3LC$ excited states with some ligand-to-ligand charge transfer (3LLCT) character depending on the auxiliary ligands. Strong field ligand coordination is desirable because it rises the energy of the nonradiative dd metal centered excited states causing enhancement of the quantum yields.

Following the interest of the group in designing photoluminescent cyclometalated systems based on strong field ligands such as CN^- , isocyanide or acetylide,^{2,3} here we present the synthesis and optical properties of a new family of neutral cyclometalated iridium(III) heteroleptic complexes $[Ir(C^*N)_2(CNXyl)(C\equiv CR)]$ (C^*N = difluorophenylpyridinate (dffpy) **1**, 2-phenylbenzothiazolate (pbt) **2**, 2-phenylquinolate (pq) **3**; R = *p*-tolyl **a**, $C_6H_2(OMe)_3$ **b**, pyrene **c**). These complexes are luminescent in different media, originating from $^3MLCT/^3LLCT/^3LC$ states, as supported by TD-DFT studies.

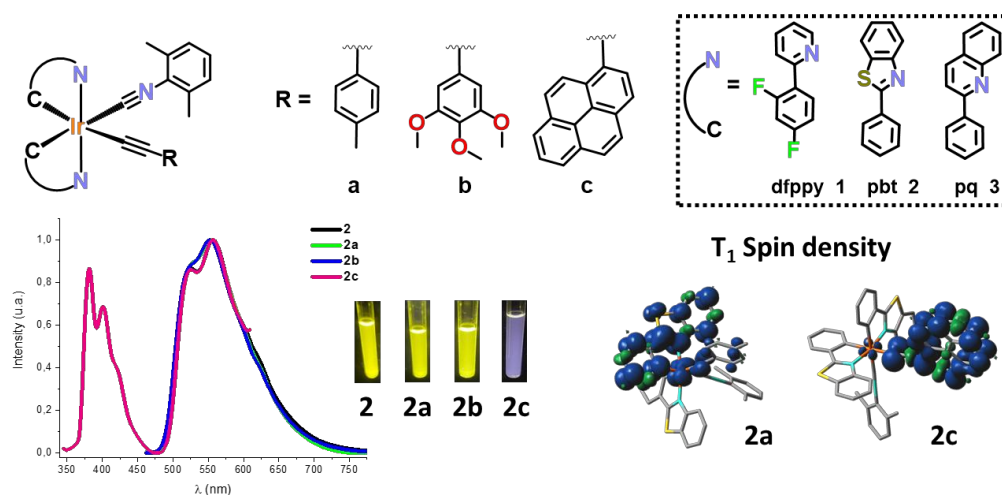


Figure 1: Synthesized cyclometalated Ir(III) complexes with different acetylide ligands.

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3D-PRINTED EOSIN Y-BASED HETEROGENEOUS PHOTOCATALYST FOR ORGANIC REACTIONS

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Photoredox catalysis for organic transformation has been considered as a powerful tool in organic synthesis since its revival in 2008 [1-2]. This innovative field of chemistry relies on the excitation of a photocatalyst (PCat) giving an excited state with unique properties, including the ability to transfer electrons or to transfer energy. However, most of the photocatalysts are prepared and used in homogeneous phase which limits the applications since the photocatalyst is not recover at the end of the reaction. The solution is to switch from homogeneous to heterogeneous catalysis using a support with high accessibility to PCat [3-4]. The approach of this project is the fabrication and evaluation of new 3D printed polymer-based supported photocatalysts [5-6]. Polymeric supports are synthesized via free radical polymerization to yield a recyclable hierarchical polymeric network including a non-toxic PCat (eosin Y) covalently bounded. The photocatalytic activity of this new object was then evaluated through model organic reactions in oxidation, reduction, and photosensitization.

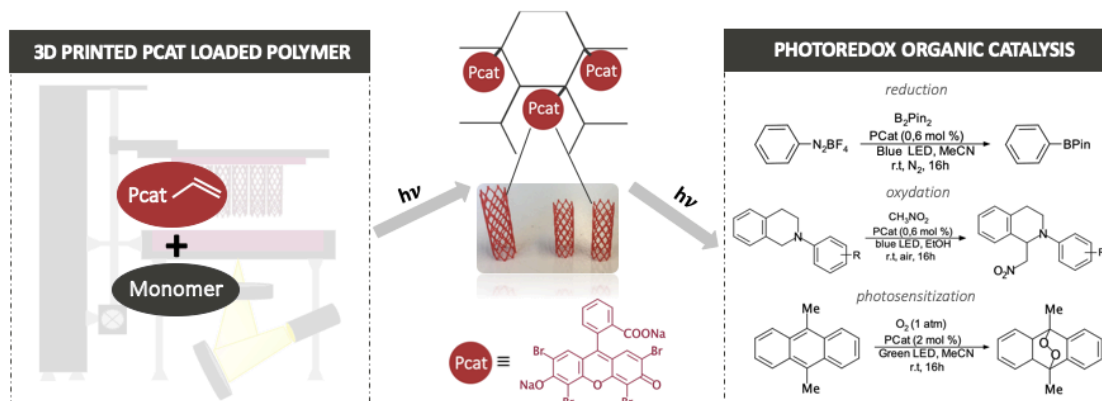


Figure : 3D-Printed heterogeneous photocatalyst for organic reactions.

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3D printing of micro-actuators made of liquid crystal.

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Humankind always sought to create tools which allow the accomplishment of tasks that would be difficult or couldn't be done otherwise. Reproduction of simple movements observable in nature often require the design of complex tools but that are limited in terms of degree of motion in particular at the micrometric scale[1]. Among many microfabrication methods, two photons polymerization (TPP), dedicated in the realization of 3D-microstructures, appears as a prime position technique to create new tools. Thus, microrobots fabricated by TPP have been conceived for applications in nanomedicine, allowing to consider new strategies for the targeted release of drugs in the system[2] or even in vitro fecondation[3]. This work aims to fabricate micro-devices made of liquid crystals with different molecular alignments. We used a new technique to programme at the microscale the molecular conformation in 3D and thus the deformation of our material. Upon heating the sample go from a single design to several possible deformation (closure, twist...).

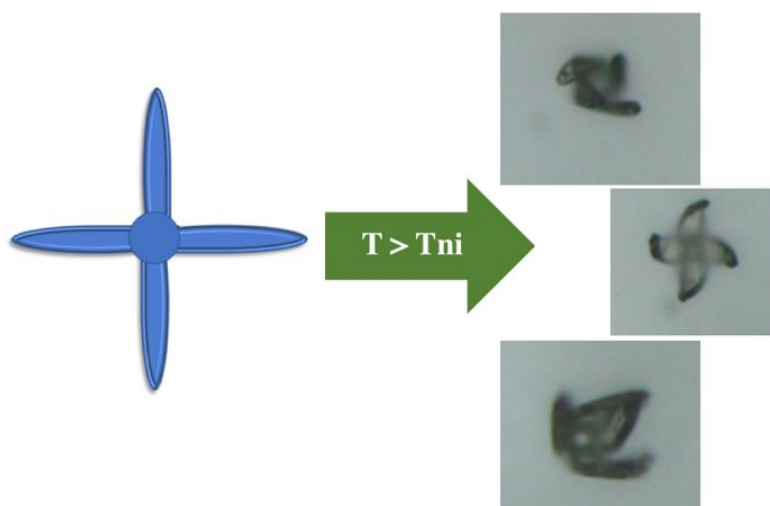


Figure 1 : Micro-clamps with different deformations upon heat.

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CRITICAL FACTORS DRIVING FOSTER RESONANT ENERGY TRANSFER BETWEEN QUANTUM DOTS

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Förster Resonant Energy Transfer (FRET) is a physical phenomenon involving the non-radiative energy transfer between two fluorescent species. More precisely, such a dipole-dipole energy transfer occurs from the excited state of a donor to a lower-energy state of an acceptor. One of the most interesting application of FRET relies on the development of highly sensitive optical biosensors. In such FRET-based biomedical devices, the donor entity is usually an organic fluorophore or a semiconductor quantum dot (QD) while the acceptor entity is always an organic fluorophore. There is only a few works where QDs are used as acceptors. The reason stems in their broad absorption spectrum which is responsible of an important emission background signal hindering the FRET detection.

We recently showed the possibility to use QDs both as donors and acceptors to achieve efficient FRET and fabricate efficient biosensors based on this phenomenon.¹ Figure 1 highlights the proof of concept. Especially, we studied both experimentally and theoretically the FRET mechanism occurring within pairs of QDs having different emission wavelengths in order to determine the critical factors driving the process. First, using fluorescence spectroscopy, we determined the donor fluorescence quenching rates (DFQR) and the acceptor fluorescence enhancement factors (AFEF). Second, we developed a mathematical model based on the energy diagrams of two coupled QDs and their relaxation paths. The model fits well the DFQR and AFEF experimental values and allowed us to identify the key parameters driving FRET in the specific case of QDs: the number of donors per acceptor, their absorption cross sections, the dissipative coupling of the QDs with their surrounding medium and the difference between the QDs fluorescence wavelengths.

Our work opens new ways for the development of efficient all-QD based biosensors.

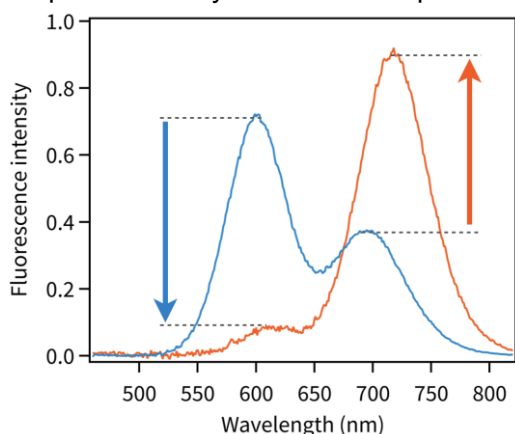


Figure 1: Fluorescence spectra of QDs solutions when FRET occurs (red curve) or not (blue curve). The process is highlighted by the decrease of the donor fluorescence band and the increase of the acceptor one.

Acknowledgements

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Growth of Ge nanoribbons on Al(110)

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Since the breakthrough of graphene in 2004, a new field of low dimensional materials in solid state physics were extensively studied, especially silicene and germanene, two allotropic 2D structures of silicon and germanium, respectively. Only a few studies have focused on one dimensional structures like silicon or germanium nanoribbons [1][2][3]. In this work, we have successfully fabricated germanium nanoribbons for the first time on a Al (110) substrate surface. After deposition by molecular beam epitaxy (MBE) one monolayer of Ge at low temperature (below 100°C), the low energy electron diffraction (LEED) pattern shows the non-reconstruction of the substrate surface, in addition, an elongation of spots along the [-110] direction is observed indicating the growth of one-dimensional objects along the perpendicular [001] direction. The scanning tunnelling microscope (STM) images show regular parallel nanoribbons on the surface (Fig. 1). Using X-ray photoelectron spectroscopy (XPS) before and after Ge deposition, we have controlled the surface and followed the dynamics of the nanoribbons coverage process (Fig. 2).

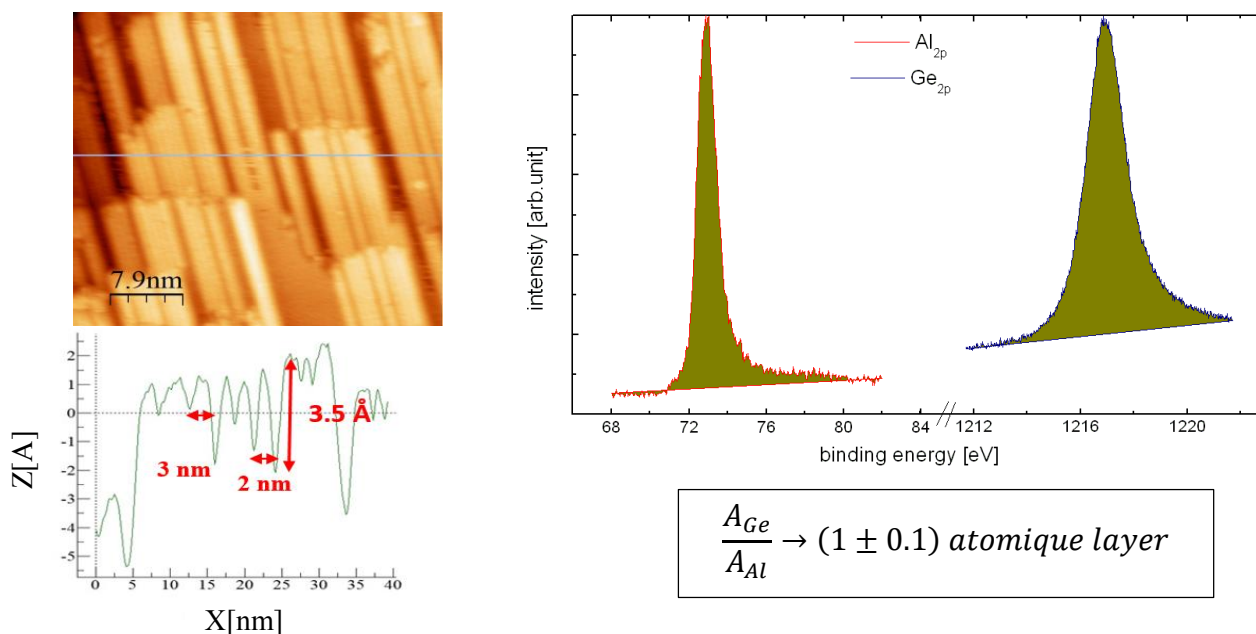


Figure 1 : Topographic STM image of nanoribbons after deposition of 1 ML Ge on Al(110). ($V = +2$ V, $I = 50$ pA)

Figure 2 : photo-excited core level lines of Al_{2p} and Ge_{2p} with coverage calculation via lines areas

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ORANGE- AND RED-EMITTING NEUTRAL HETEROLEPTIC COPPER(I) COMPLEXES WITH PYRROLATE SCHIFF BASE DERIVATIVES

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Luminescent copper(I) complexes are nowadays extremely appealing from a technological point of view to be employed for advanced applications such as organic light emitting diodes (OLEDs). Other possible applications include photocatalysis and photopolymerization reactions.¹

Herein, we report the synthesis and characterization of orange- and red-emitting neutral heteroleptic copper(I) complexes having pyrrolate Schiff bases as chelating N-donors. The ligands were synthesized by condensation reaction in presence of 4Å molecular sieves (Tagouchi's method). Triphenylphosphine, DPEphos and Xantphos were used as mono- and bidentate phosphine. The complexes were synthesized starting from CuCl, the chosen phosphine and the deprotonated Schiff base obtained by reacting *in situ* the imine with KO^tBu. The derivatives were isolated as intense yellow powders owing to the presence of MLCT bands, as further confirmed by UV-vis spectroscopy. The structure of most of the complexes was unambiguously determined by means of X-ray diffraction. Upon excitation with near-UV and violet light, the derivatives exhibited orange and red emissions with emission maxima, photoluminescent lifetimes and quantum yields strongly influenced by the chosen N- and P-donor ligands. The emissive properties were investigated by means of DFT and TD-DFT calculations, revealing the scarce involvement of the phosphine in the ³MLCT mechanism. The complexes will be tested for the free radical photopolymerization of pentaerythritol triacrylate (PETA) in presence of diphenyliodonium hexafluorophosphate (Iod).

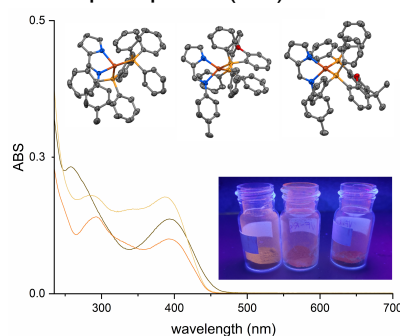


Figure: UV-vis spectra and X-ray structure of selected copper(I) complexes. Inset: Picture of the complexes under UV light.

Acknowledgements

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PLASMONIC INKS WITH CHAMELEON EFFECT

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Due to the vibrant colors produced by their interaction with visible light, metallic nanoparticles have been used for centuries by artists. Nowadays, colloidal nanoparticles have shown interest mainly due to their strong size and shape-dependent properties. Indeed, metallic nanoparticles, synthesized by oxidation-reduction reaction, can appear colored by a phenomenon of surface plasmon resonance.

Moreover, the chameleon can produce and modulate its color thanks to the guanine crystals present in its epidermis. By analogy, the plasmonic effect, induced by nanoparticles, is influenced by the interparticle distance. Based on that principle, mechanical or chemical stress can induce, in the material, a color change by reproducing or increasing the particles spacing.

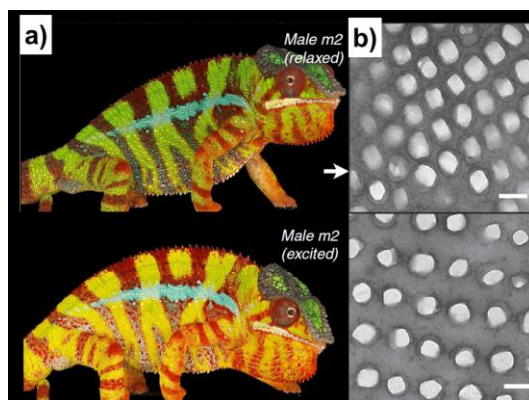


Figure: The chameleon capable of changing its skin color explain by guanine crystal distance: (a) macroscopic color change and (b) microscopic correspondence.

Current formulated BIC inks are colored using dyes and pigments. This project focuses on providing a new generation of more sustainable and environmentally friendly coloring agents by exploiting the plasmonic effect which characterizes metallic nanoparticles.

Different nanoparticles synthesis methods using chemical batch and continuous flow processes, have been developed and discussed in this study. Finally, these results open new routes to create inks allowing to generate fixed colors and color changing, inspired by nature.

Acknowledgements: BIC Ecriture 2000, CNRS, IS2M, Université de Haute Alsace.

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Reductive Activation of aryl chlorides by organophotoredox catalysis

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In the last decades, phenothiazine derivatives established themselves as strongly reducing organophotoredox catalysts in photochemistry. Electron-rich phenothiazine derivatives could be synthesized with strong reduction potentials. Especially 4-(*N,N*-diisobutylaminophenyl)phenothiazine **2** and 4-(*N,N*-diisobutylamino-2,5-dimethylphenyl)phenothiazine (**3**) have a redox potential of $E_{ox}(2^+/2^*) = -2.9$ V vs. SCE and $E_{ox}(3^+/3^*) = -3.0$ V vs. SCE.^[1] Due to the extremely strong reduction potential in the excited state of this catalysts, photoredox catalytic activation of aryl chloride could be achieved. Aryl chlorides exhibit a reduction potential of -2.8 V vs. SCE because of their very stable C(sp²)-Cl bond with 97 kcal/mol. This homolytic cleavage enabled photocatalyzed borylations, Arbuzov reactions and arylations. Moreover, these photoredox catalyses are characterized by a high substrate scope of aryl chlorides possessing both electron-withdrawing and electron-donating substituents.

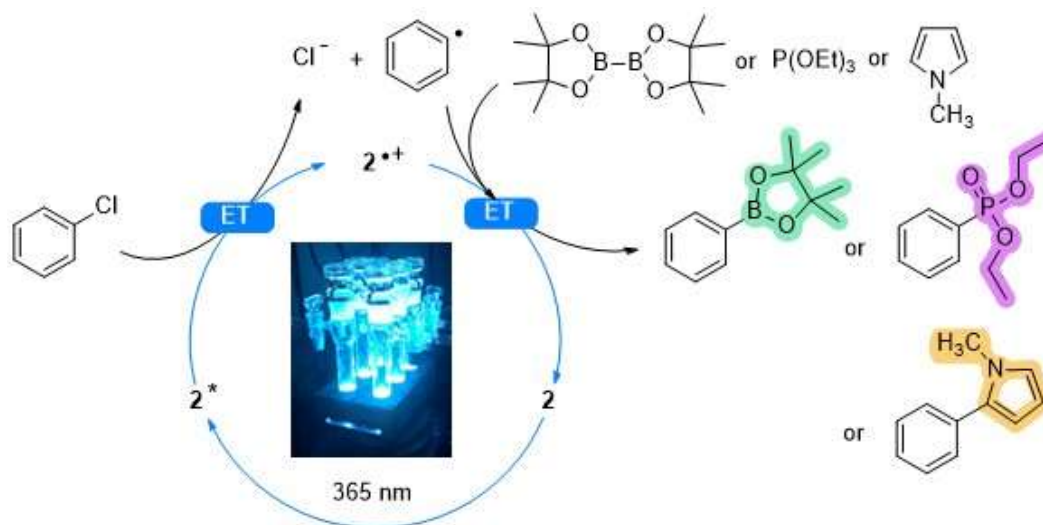


Figure: Principle photoredox catalytic cycle for the activation of chlorobenzene to the aryl chloride and formation of the borylated, phosphonylated and arylated products.

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Hemipiperazines As Novel Peptide-Derived Molecular Photoswitches

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Using light as a trigger to reversibly change the geometry of molecules has gained a lot of interest in recent years, not least because of its high degree of selectivity and orthogonality. Molecules that react upon light illumination with an alteration of their geometry are known as molecular photoswitches and have thus far been employed in a broad range of varying research context, e.g. data storage, material science and biochemistry. Especially employing molecular photoswitches as dynamically addressable bioactive compounds has been demonstrated numerous times to be a promising lead for groundbreaking pharmacological advancement.

Our group discovered a new class of molecular photoswitches – hemipiperazines (HPI) – in the structure of a potent antimitotic agent and an anticancer drug candidate plinabulin. This photosensitive structure enabled photomodulation of its bioactivity over 2-3 orders of magnitude. The HPI photochrome consists of an arylidene group attached to the 2,5-diketopiperazine ring, which can undergo light-induced reversible *E/Z*-photoisomerization.

Here, we report the in-depth photophysical investigations of HPIs, which have been shown to be water-compatible and able to withstand physiological reductive conditions over multiple switching cycles. Further, HPIs exhibit high selectivity in addressability of either isomer, in some cases even near-quantitative photostationary states, as well as very long thermal-half lives of the metastable isomers. In combination, these properties make HPIs very favorable candidates for chromophores in the field of photopharmacology and smart materials.

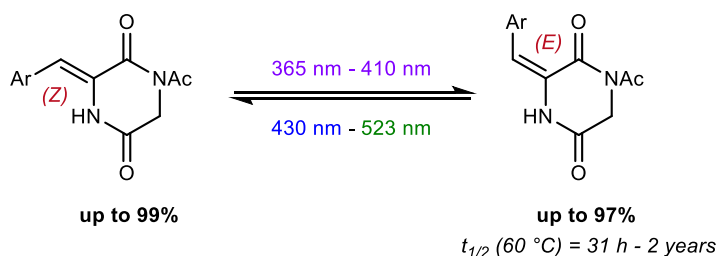


Figure 1: General structural motif of HPIs and outline of their photophysical properties.

Our poster will depict the recent progress in analysis and applications of the novel photochromic HPIs based on carbocyclic as well as heterocyclic arylidene substituents of the cyclic dipeptide motif.

Acknowledgements

We acknowledge the financial support of DFG (Grant 1124/6-3, GRK 2039) and the Jürgen Manchot Stiftung.

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SYNTHETIC AND OPTICAL STUDIES OF NEW CYCLOMETALATED Pt^{IV} COMPOUNDS WITH CHELATING N,N'-DONOR LIGANDS

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In contrast to the numerous studies carried out on d⁶ (Ir^{III}, Ru^{II} or Os^{II}) and d⁸ phosphors (Pt^{II}, Au^{III}), the related on Pt^{IV} derivatives are scarce¹. Recently our group has published new series of neutral bis(cyclometalated)pentafluorophenyl Pt^{IV} complexes bearing Cl⁻ or CN⁻ as ancillary ligands². Benzothiazole has demonstrated to be a good platform employed as ligand to obtain yellow phosphorescent metal complexes with myriad applications as biosensing, optical devices, photocatalysis or chemotherapy.

In this topic, we present a new series of dicationic bis-cyclometalated Pt^{IV} compounds of type [Pt(pbt)₂(N[^]N)]Q₂, bearing 2-phenylbenzothiazole (pbt) as cyclometalating ligand and chelating N,N'-phenanthroline-based ligands (N[^]N = phen **4**, pyraphen **5**, NH₂-phen **6**), with two different counteranions (Q = PF₆, CF₃CO₂), using [Pt(pbt)₂Cl₂] **2** and [Pt(pbt)₂(OCOCF₃)₂] **3** as starting materials. The *trans*-N,N *cis*-C,C configuration was confirmed by X-Ray diffraction analysis of complexes **2**, **3** and **4-PF₆**. Optoelectronic properties in different media (solid state, solution and doped polymeric films) have been studied with the support of theoretical analysis at DFT/TD-DFT level for all complexes. Complexes **2** - **5** exhibit pbt-centered (³IL) emissions, whereas dual emission associated to two close different, ³IL'CT (L'=NH₂-phen) and ³IL(pbt), states was found for the NH₂-phen complex **6**.

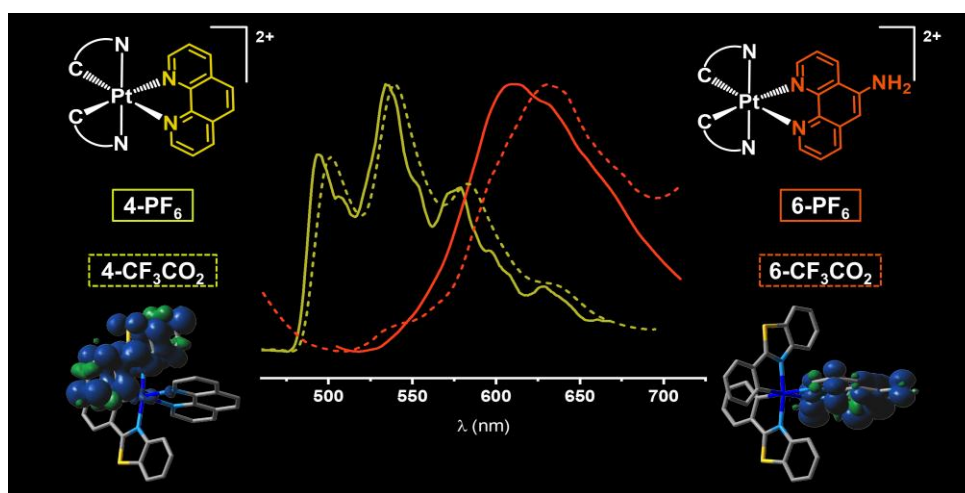


Figure 1: Structure, emission (CH₂Cl₂, 77 K) and spin density of the T₁ optimized state for **4** and **6**.

Acknowledgments: We thank Spanish Ministry of Science and Innovation (Project: PID2019-109742GB-I00) for financial support. D.G S is grateful to UR for a PhD grant.

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Formation of CPD damage in DNA via energy transfer by Xanthenes as photosensitizer

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Solar UV light can be a threat to DNA and leads to light-induced DNA damage, which in the worst case can lead to cancer. Cyclobutane pyrimidine dimers (CPDs) are the most abundant photodamage in DNA and are known to be an origin of skin cancer. In addition to direct UV excitation, CPD formation occurs also indirectly via energy transfer mechanisms triggered by sensitizers such as Xanthenes.^[1,2,3] By synthesizing the respective sensitizers as phosphoramidites, they can be incorporated into the DNA via phosphoramidite-synthesis. Through specific DNA hybridisation, the sensitizers can be placed at defined distances to the resulting CPD damage, which allows studies on the distance dependent CPD formation as well as on the mechanism of the resulting energy transfer.

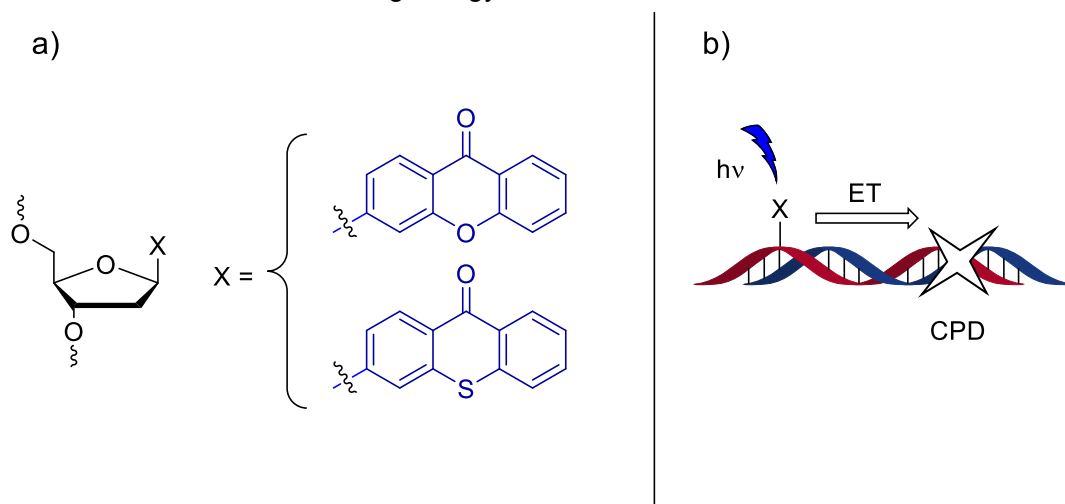


Figure : a) X = Xanthone and Thioxanthone as sensitizers incorporated into the DNA. b) Simplified representation of energy transfer (ET) through DNA leading to CPD formation.

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Recently proposed oxime-ester as blue- light-sensitive type I photoinitiators

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Photochemical engineering of polymers and other modern materials science and technology has led to the creation of complex but effective methods for the fabrication of innovative materials, post-functionalization of polymers and novel synthetic products. In these systems, light-activated chemical reaction pathways not only provide an excellent control over the reaction kinetics but also make it simple to carry out complex synthetic protocols. [1-3] However, the search for more ecologically friendly photoinitiating systems that can be activated with visible light is currently under progress. At present, a wide range of two- or three component photoinitiating systems with absorption spectra perfectly matching the emission of LEDs is available. Hence, in order, to create more easily free radicals directly by the cleavage of chemical bonds, one-component Type I PIs are now preferred. In this context, the high reactivities of oxime esters (OXEs) as Type I photoinitiators in free radical photopolymerization are well known. For these structures, light irradiation can lead to the homolytic cleavage of the N-O bond, generating iminyl and acyloxy radicals. [4] Several research studies have been published in recent years, with the purpose of modifying their chemical structures by introducing different chromophores or by varying the substitution pattern of the ester group, for which an interesting structure/reactivity/efficiency relationship could be achieved. In this work, an overview of the recent advances on oxime-esters based photoinitiators, as well as a comparison of the various scaffolds proposed is provided and discussed.

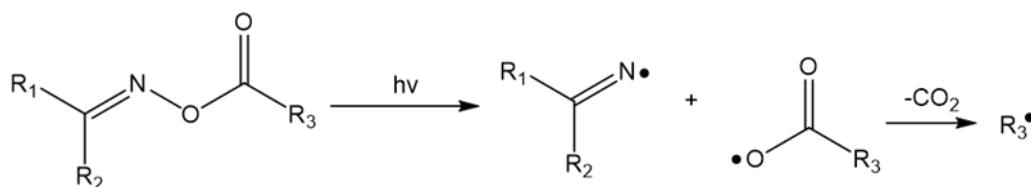


Figure : Photochemical mechanisms for oxime-esters.

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DYE PHOTODEGRADATION UNDER VISIBLE-LIGHT BY NANOESTRUCTURATED HYBRID ORGANOMETALLO-TITANIAS

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TiO₂ has become one of the most popular nanostructured semiconductor material because of its excellent properties such as availability, low toxicity, high stability and good catalytic activity. However, titania has a high electronic bandgap between the valence and conduction bands (about 3.2 eV). For this reason, it is only active under UV light. To solve this problem and get titania active under visible light, our group has developed an *in-situ* method based on the so-called *Sol-Gel Coordination Chemistry* (Figure 1.1).^[1] With this aim, two nanostructured organometallo-titania hybrid materials, **[1]-TiO₂** and **[2]-TiO₂**, have been synthesized from two Ir(III) complexes: [Ir(ppy)₂(3,3'-H₂dcby)](PF₆) (**1**)^[2] and [Ir(ppy)₂(4,4'-H₂bicinchoninic)](PF₆) (**2**), respectively (Figure 1.2). These materials have been shown to be very stable and efficient photocatalysts under visible-light irradiation in the degradation of Rhodamine 6G in aqueous media. Although both materials are more efficient than control titania (TiO₂) under blue and white light illumination, **[2]-TiO₂** shows higher kinetic constants than **[1]-TiO₂**; specially under white light illumination, where **[2]-TiO₂** is six-fold more efficient than **[1]-TiO₂** in the same reaction conditions (Figure 1.3).

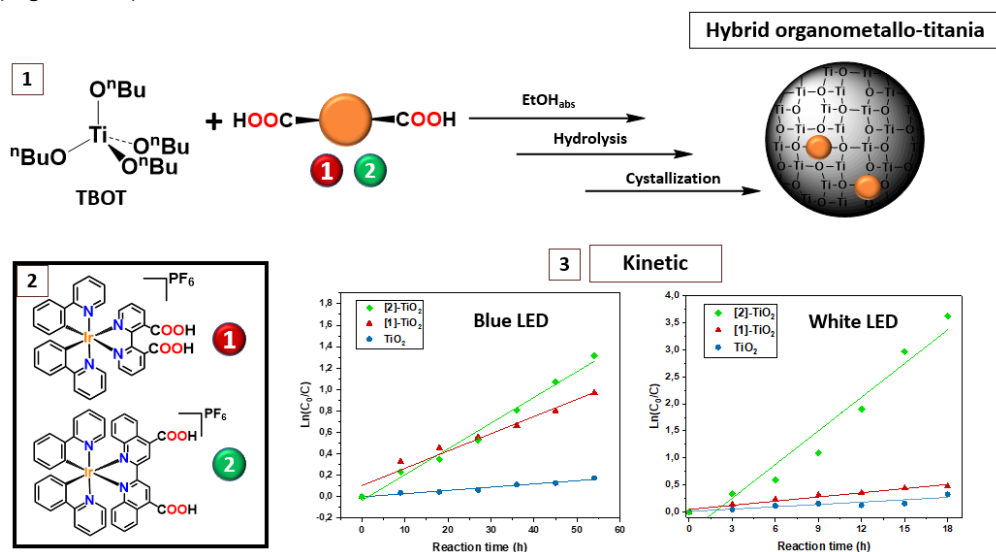


Figure 1: 1) *Sol-Gel Coordination Chemistry*. 2) Ir(III) complexes. 3) Photodegradation kinetics of Rhodamine 6G in aqueous solutions using the nanostructured materials under blue and white LED illumination.

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THE GROUND AND EXCITED STATE ABSORPTION OF TRIPHENYLAMINE (TPA) AND DIMETHYLMETHYLENE-BRIDGED TRIPHENYLAMINE (DTPA): A QUANTUM-CHEMICAL STUDY

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Triarylamine derivatives have been used as hole transport and hole injection materials for OLEDs and perovskite solar cells. It was found that π -conjugation has a significant impact on the properties of triarylamine derivatives.¹ The understanding of the effect of planarization on the excited state dynamics is a key factor for the development of more efficient optoelectronic devices.

As a powerful tool, transient absorption (TA) has been applied to analyze photophysics in complex systems and study excited states processes. However, the analysis of TA signatures is usually tedious owing to the complexity of spectral features; thus, in many cases, the assignment is nontrivial to handle and requires in-depth quantum chemical investigation.² In this work, TPA and DTPA were taken as representative examples for a TDDFT study to shed light on the effect of π -conjugation on the excited state dynamics. The intermediates such as transient *N*-phenyl-4*a*,4*b*-dihydrocarbazole (DHC₀) and the corresponding excited-state absorption signals were characterized, which show good agreement with the transient absorption experiments.

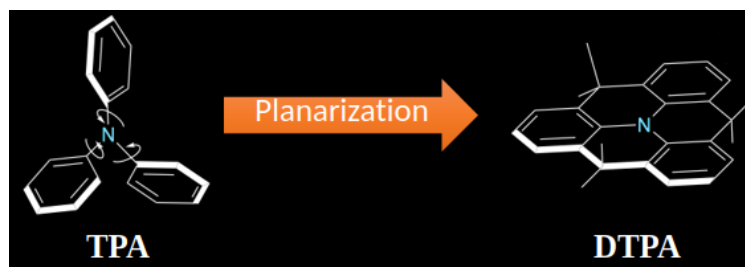


Figure 1: Triphenylamine (TPA) and dimethylmethylene-bridged triphenylamine (DTPA).

Acknowledgements

The authors thank the Sonderforschungsbereich SFB 1249 of the German Science Foundation for funding as well as the Chinese Scholarship Council for a Ph.D. Scholarship. We also thank Jie Han, Nils Oberhof, Anna Weidlich, Lin Tian and Hendrik Brockmann for valuable ideas and discussion.

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ESTIMATION OF WATER CONTENT IN MICROGELS USING SUPER-RESOLUTION FLUORESCENCE LIFETIME IMAGING

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Water molecules play an important role in the structure, function, and dynamics of (bio-)materials, and an estimation of the number of water molecules inside different compartments is thus important. It was reported that, in presence of H₂O, the fluorescence of red emissive dyes like Atto 655 is quenched by transferring the excited energy to the surrounding H₂O molecules.^[1] Exchanging H₂O by D₂O increases the fluorescence quantum yield and concomitantly also increases the fluorescence lifetime. Fluorescence lifetime imaging (FLIM) can thus be used to count water molecules around the reporter dye Atto 655, which in our study was covalently embedded into microgels, an interesting class of nanoparticles with high potential in drug delivery, medicinal chemistry, and biochemistry.^[2,3] We recorded FLIM images in different H₂O:D₂O ratios in the swollen state of the microgels at 22 °C and in their collapsed state at 40 °C. Stern-Volmer analysis allowed us to calculate the number of water molecules in the direct surroundings of the dye molecule inside the microgels at different temperatures. Additionally, the combination of FLIM with localization-based super-resolution microscopy allows for an estimation of the spatial distribution of water inside microgels.^[4,5]

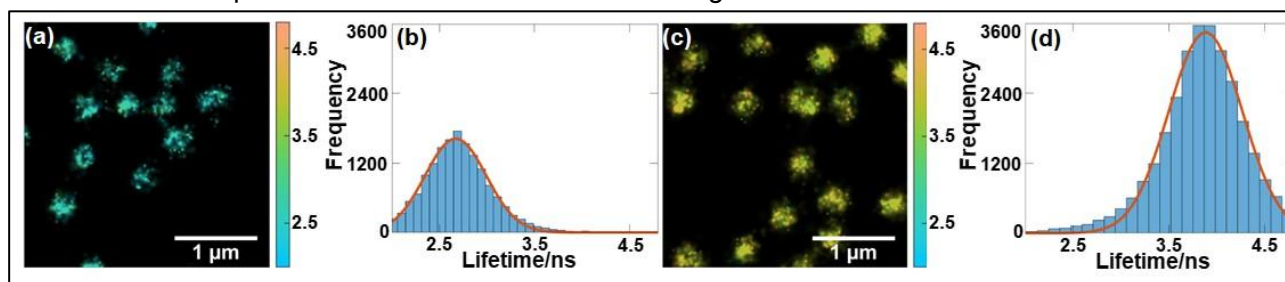


Figure 1: (a) and (c) are super-resolved FLIM images of Atto 655 labelled microgel in H₂O and D₂O, respectively. Color scales indicate lifetime in ns. (b) and (d) are corresponding lifetime distributions with Gaussian fitting.

Acknowledgements

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NIR photopolymer for micro-optics applications

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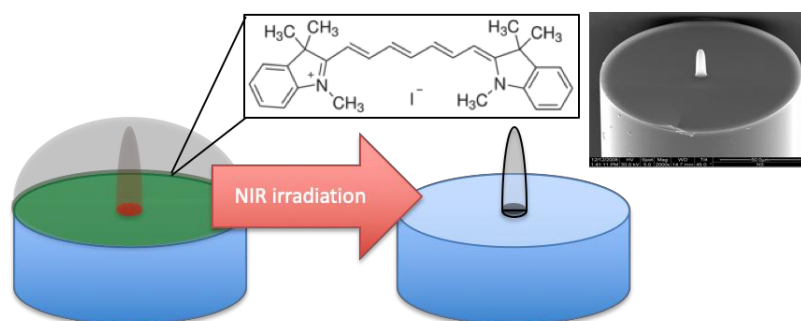
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Near infrared (NIR) activable photopolymers suitable for versatile fabrication of micro-optical elements were developed. The first main objective is to show that these new photopolymers can be used for microfabrication and investigate the parameters governing the microfabrication process. The impact of photonic, physico-chemical and chemical parameters is discussed. High quality microstructures with a good control over their size and shape are demonstrated. The second main objective is to show practical examples of microlenses and waveguides implemented on single core and multiple core optical fibers, VCSELs, and glass slides are then presented. The NIR photosensitivity of this negative tone photoresists allows using the device source itself as to start the crosslinking process, which constitutes a convenient approach for micro-optics self-positioning on NIR sources and justifies the interest of such NIR photopolymer for the fabrication micro-optical elements and optical interconnects.



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CAPILLARY FORCE DRIVEN SELF-ASSEMBLY OF 3D PRINTED HIERARCHICAL STRUCTURES PREPARED BY TWO-PHOTON POLYMERIZATION

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Hierarchical structures in nature have inspired numerous applications in chemistry, biology, optics, and mechanics, as well as in scientific research and technical implementations [1]. Among many microfabrication techniques, two-photon polymerization (TPP) is well established as a method for creating complex 3D micro-objects with stimuli-responsive and reconfigurable surface properties [2,3]. TPP-based laser printing capillary-assisted self-assembly (LPCS) strategy appears as a prime position technique for fabricating periodic structures [4]. A hierarchical microstructure that is highly controllable can be generated by using capillary force to drive straight pillars as shown in Figure 1.

This work aims to fabricate periodic hierarchical architectures through two-photon laser polymerization and controlled capillary force assembly by solvent evaporation. Various assemblies of micropillars with different configurations can be achieved by adjusting the height, arrangement, and laser power and printing speed of micropillars to guide capillary force. This mechanical tunable self-assembly of microstructures can be used for surface modification applications, micro-optics, and microfluidics.

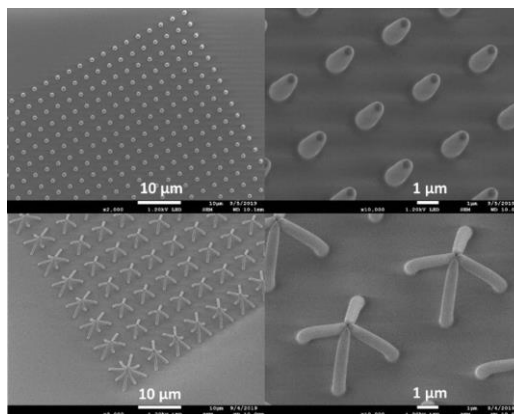


Figure 1: Controllable capillary force assembly of micropillars. (A) Top and tilted SEM view of 3D-printed micropillars obtained by using supercritical CO₂ dryer. (B) Top and tilted SEM view of capillary-assisted self-assembly micropillars.

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Integration of nanostructured sensor for the electrochemical detection of biomarkers: towards search for life in space

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Nowadays, metallic nanoparticles with various shape have been largely used for the fabrication of new sensors due to their fascinating properties. One particular shape has attracted much attention because of its large surface-to-volume ratio and high sensitivity: the dendritic nanostructures. These anisotropic nanoparticles are often made of noble metals, such as gold that owns a good biocompatibility and high plasmonic effect¹.

The present work describes a controlled growth pattern-directed organisation of gold flower-like crystals deposited onto gold quartz QCM resonator to achieve large-scale nanostructured surfaces of detection. This technique consists first, in the deposition of a nanoporous polymer template, on which gold crystals are electrochemically grown. Then, the adsorption of amino acids on those structures can be realized by different ways. The detection of the adsorbed molecules onto these nanostructured surfaces, has been carried out optically and electrochemically.

The last step of this work focuses on the regeneration of the substrate that allows the recovery of the sensor to its initial state to continue another cycle of detection of molecules. This device is a first step before its integration in a lab-on-chip system.

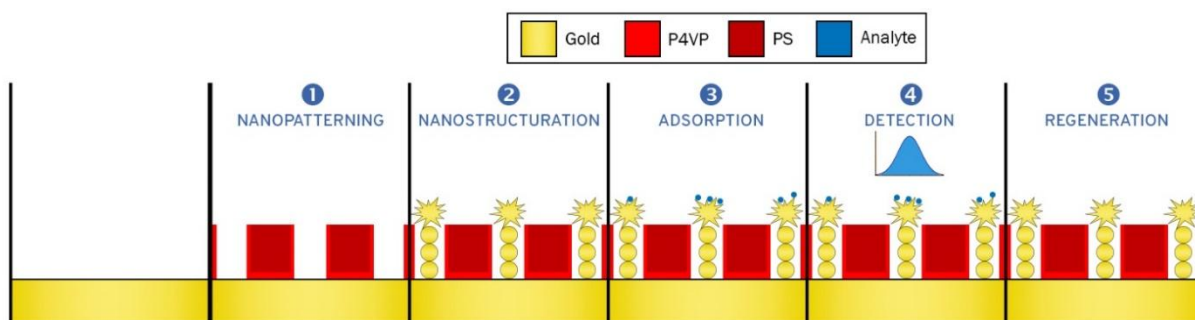


Figure 1: The different steps of the sensor development based on gold nanoparticles and gold QCM resonator.

Acknowledgements

CNES and CNRS

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Anisotropic functionalization of gold nanoparticles by optical near-field photopolymerization

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The interaction of light with metallic nanoparticles (MNPs) induces an oscillation of the conduction electrons, giving rise to a localized surface plasmon resonance (LSPR), which generates a local enhancement of the electric field around the nanoparticles. This effect can be used for local functionalization of the nanoparticles by photopolymerization via the enhancement of the electromagnetic field [01]. The electric field distribution can be controlled anisotropically by two parameters, the polarization of the excitation light and the shape of the AuNPs. For a fixed shape of MNPs, the polarized excitation allows the selection of one plasmonic mode over the others by discrimination, while the shape anisotropy allows the selection of one of the plasmonic modes under fixed polarization [02].

In this work, gold nanoparticles (AuNPs) of different shapes (triangles, rods, bipyramids and discs) are used to study the plasmonic electric field distribution around these AuNPs under polarized and continuous or pulsed excitation. This study will be carried out on transmission electron microscope (TEM) grids, the hybrid nanoparticles are observed in TEM before and after anisotropic functionalization, and the experimental results are correlated with simulations.

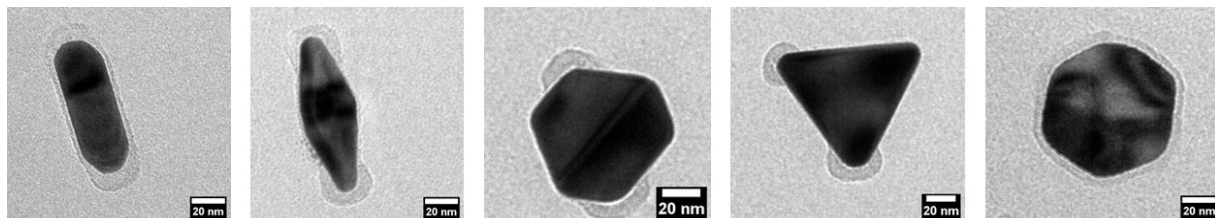


Figure: Near-field anisotropic functionalization of gold nanoparticles by two-photon photopolymerization

Acknowledgements

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Functionalization of the SERS platform with molecularly imprinted polymer using localized surface plasmon resonance for sensitive detection

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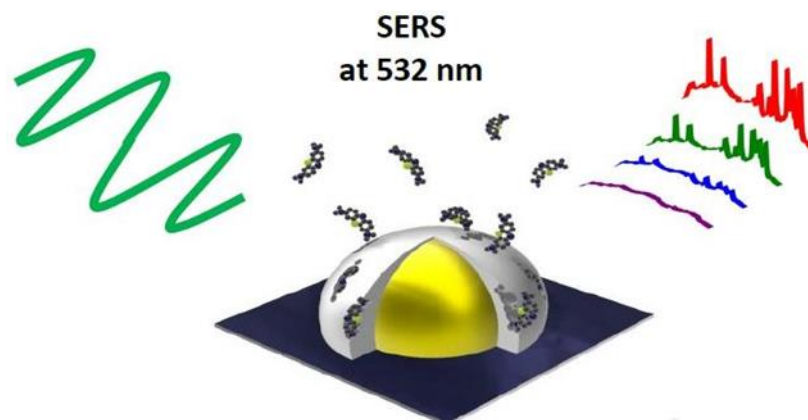
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A new simple, fast and versatile method for the functionalization of gold nanoparticles (AuNPs) by a nanoscale layer of molecularly imprinted polymers (MIPs) was developed ¹. The key step is based on near-field radical photopolymerization ² of a MIP pre-polymerization mixture ³. This allows the preparation of hybrid AuNPs@MIPs nanoparticles which are used as substrates for LSPR and surface enhanced Raman spectrometry (SERS) analyses with excellent sensitivity and specificity. To demonstrate the performance of AuNPs@MIPs, MIPs specific to methylene blue (MB) were prepared. The sensitivity of spectroscopic detection is in the range of 10 nM. Specificity is demonstrated by comparing the response with a control non-imprinted polymer (NIP) and by interference tests with two analogues (Rhodamine 6G and Rhodamine 110) ¹. This fabrication method allowed us to obtain robust and recyclable sensing surfaces with high sensitivity and selectivity. The nanometric thickness of MIP allows a short analysis time (10 min), which improves the performance of MIP-based sensors and opens new perspectives to detect molecules at very low concentrations.



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Photocatalytic activation of SF₆: Scoping for the limit of the substrate spectrum

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The importance of SF₅ functionalized molecules increases due to their application in pharmacy or in optoelectronics. [1,2] In the past, the synthesis of pentasulfanylated molecules often meant working with toxic compounds like SF₅Cl or SF₅Br. The photocatalytic activation of sulfur hexafluoride (SF₆) makes obtaining SF₅-functionalized molecules possible starting from diphenyl ethylene- and styrene-derivatives without adding toxic SF₅Cl/Br. [3,4] To better understand the influence of different properties of the starting material on this reaction and to expand the substrate scope should be extended for further follow-up chemistry. For this purpose, various aromatic and aliphatic groups as well as heterocycles were introduced to the catalysis.

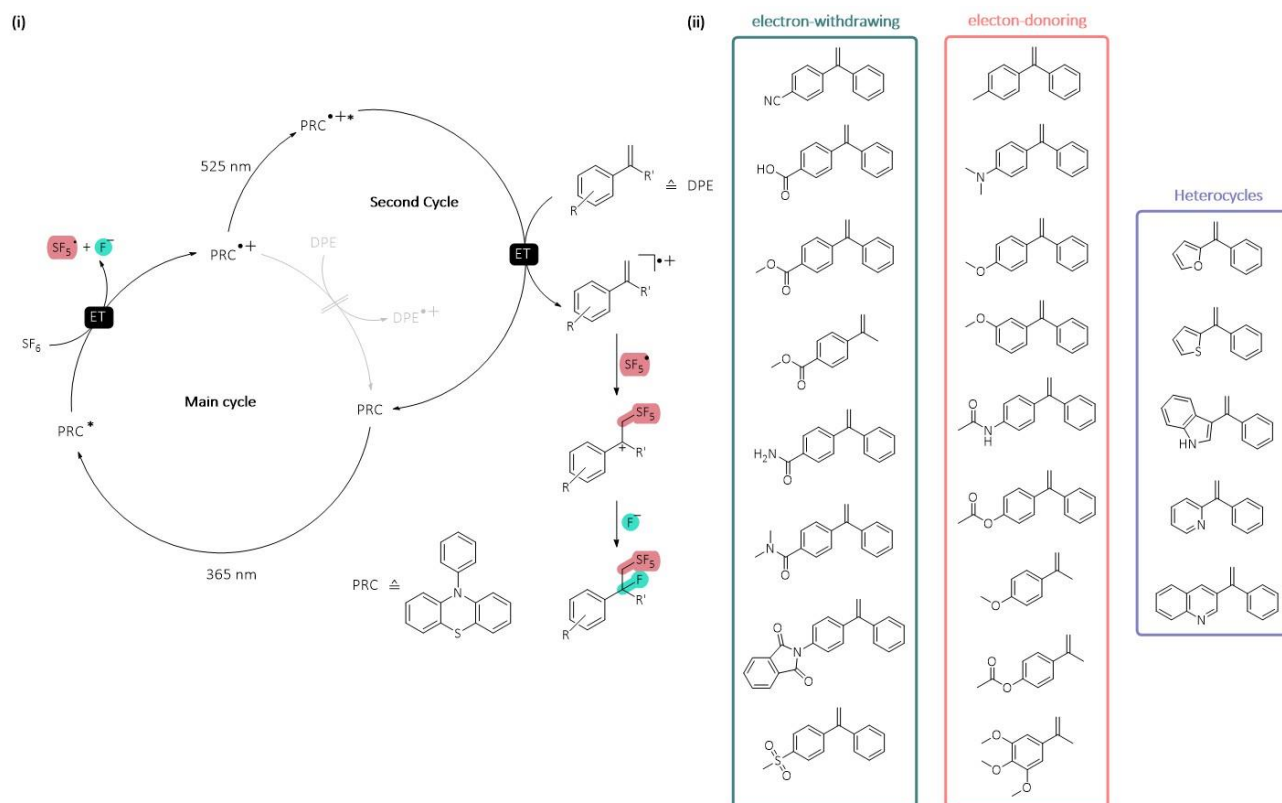


Figure: (i) schematic photoredox catalytic cycle; (ii) investigated substrate spectrum of substituents.

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Modeling phosphorescent properties of Heteroleptic Ir (III) complexes

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The d⁶ transition metals have myriad of exciting photophysical properties, especially Ir (III), which is very suitable for industrial applications such as organic light emitting diodes (OLEDs) and photocatalysts due to their photostability, limited access to nonemissive states, long-lived triplet excited state lifetime and tunable emission color through ligand alteration in the complex.¹ Although quantum chemical modelling of these properties is complicated and tedious, in our previous work we have performed similar kind of quantum chemical modelling for Pt(II) complexes.² In this contribution, we assess the computational machinery to calculate the phosphorescence properties of a large pool of heteroleptic [Ir(C[^]N)2(N[^]N)]⁺ complexes (where C[^]N is the cyclometalating ligand and N[^]N is the ancillary ligand) including their phosphorescent rates and vibronically-resolve emission spectra. Efficient computational protocols are next suggested. Specifically, different flavors of DFT functionals were benchmarked against DLPNO-CCSD(T) (Domain-Based Local Pair Natural Orbital Coupled Cluster theory with single, double, and perturbative triple excitations method)³ for the phosphorescence energies. Among the tested functionals, CAM-B3LYP outperforms the rest of tested functionals. Transition density matrix and decomposition analysis⁴ of the emitting triplet excited state enables to categorize the studied complexes into different cases, from e.g., predominant triplet ligand-centered (³LC) character to metal-to-ligand charge transfer (³MLCT).

We have also performed vibronically resolved phosphorescent spectra and rate calculations. Ir (III) complexes with predominant ³MLCT character are characterized by less vibronically-resolved bands as compared to those with predominant ³LC character. Furthermore, some of the complexes are characterized by close-lying triplet excited states, so that the calculation of their phosphorescence properties poses additional challenges. In these scenarios, it is necessary to perform geometry optimizations of higher-lying triplet excited states (i.e., T_n). The global analysis of computed emission energies, shape of the computed emission spectra, computed rates, etc. enable us to unambiguously pinpoint the involved species in the emission.

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Photo-generated diazonia for an anticancer therapy using light

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Recently, a photo-triggered intramolecular double nucleophilic aromatic substitution (S_NAr) has been discovered allowing the straightforward synthesis of the new compound **2** suitable for the development of an anti-cancer treatment. Indeed, diazonia **2** selectively stabilizes G-quadruplexes (G4) structures (Fig 1 left) and generates singlet oxygen.¹ In addition, thanks to the fluorescence of the photocyclized product **2**, its generation and localization may be followed up *in cellulo* (Fig 1 right).

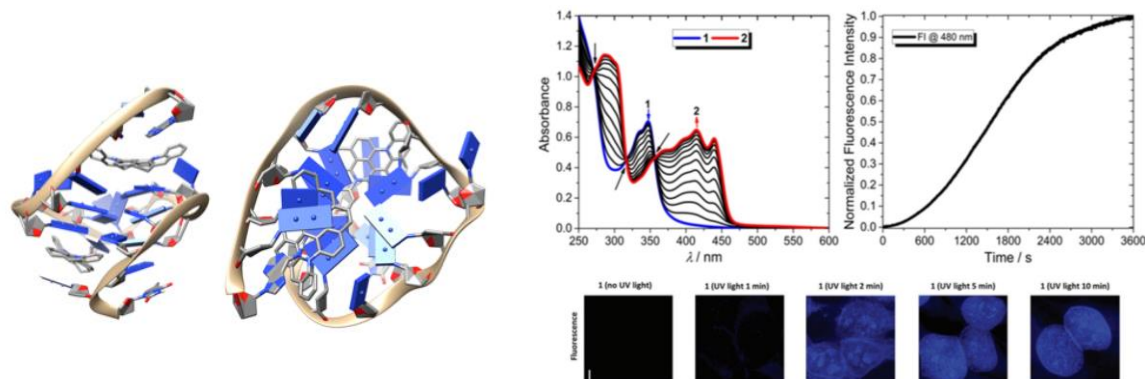


Figure 1 : Left : Representative structures of **2** in the presence of *c-MYC Pu22* G-quadruplex. Right : Photoconversion of compound **1** into diazonia **2** (in cuvette or *in cellulo*). Confocal fluorescence images of MeOH-fixed HeLa cells stained with **1** (10 μ M) upon UV irradiation.

Here, we have investigated the influence of the leaving group (Fig 2) on the photocyclization efficiency. The photoconversion quantum yield has been determined by UV-visible follow-up upon irradiation.² Therefore, we have designed a series of compounds **1** bearing a “non-innocent” leaving group linked to the aromatic core by the most efficient photolabile arms. Therefore, we are aiming at improving the pro-drug efficiency by choosing leaving groups bearing targeting groups or additional chemotherapeutic drugs inspired by photo pharmacology.³

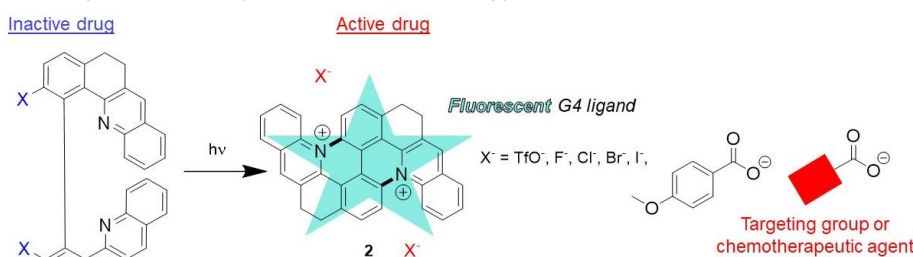


Figure 2 : Photoconversion of quinolinizinium derivatives **1** into diazonia **2** for an anti-cancer treatment.

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Water-soluble photoinitiators from dimethylamino-substituted monoacylphosphine oxide for hydrogel and latex preparation

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In order to respond to the growing demand for radiation-curable waterborne products like hydrogels or inks, there is a need for water-soluble radical photoinitiators exhibiting absorption in the near UV to visible range.^[1,2] We describe herein the synthesis of a novel type-I diphenylphosphine oxide photoinitiator bearing a 2,6-dimethyl-4-dimethylaminobenzoyl group. The presence of a tertiary amino group in the para position of the benzoyl group results in an increased absorption in the visible range and its facile conversion into water-soluble derivatives after a subsequent protonation or quaternization reaction. Quaternization with methyl triflate (MeOTf) yields a water-soluble monoacylphosphine oxide compound displaying a quaternary ammonium group $^+N(CH_3)_3$ ^-OTf . The main characteristics are water-solubility, shelf-stability, absorption in near-UV range, low cytotoxicity, and efficient α -scission as evidenced by steady-state photolysis experiments. Its photopolymerization efficiency has been evaluated by real-time Fourier transform infrared spectroscopy at 385 and 420 nm using an aqueous solution of poly(ethylene glycol) acrylate. The polymerization rate is comparable to that obtained with the conventional water-soluble monoacylphosphine oxide TPO-Li. Using this new photoinitiator, 3D-printed hydrogels and aqueous polymer dispersions can be prepared.^[3]

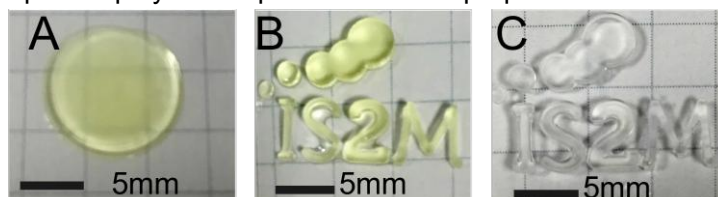


Figure . 3D printed hydrogels based prepared from an aqueous solution of PEGDA/water (50% w) using our new photoinitiator (0.8% w/w of PEGDA). Irradiation conditions: 21 mW cm⁻², 20 s. (A) the round piece, (B) IS2M logo, and (C) the same 3D-printed object after 3 days.

Acknowledgements

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Photochromic Diketopiperazine-based Supramolecular Hydrogels

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Hydrogels are soft but mechanically self-supporting materials, where a gelling agent - usually a covalent amphiphilic polymer (gelatin, agarose) – binds and cross-links large excess of water. Supramolecular hydrogels are formed either by low-molecular-weight gelators (LMWGs) or macromolecules in the presence of water, in a spontaneous and often synergistic manner by self-assembly through dynamic networks of intermolecular non-covalent bonds.^[1]

Hydrogels find application in biomedical context, and are well-known for their self-healing properties, thixotropy, on-demand reversibility and stimuli responsiveness, for example to light.^[2] These light-triggered hydrogels, also known as photochromic hydrogels, are equipped with 'photochemical switches', which give reversible molecular responses, typically in the form of *E/Z*-photoisomerizations^[3] or light-induced pericyclic reactions.^[4] Such materials are excellent candidates for photo-controlled drug release.

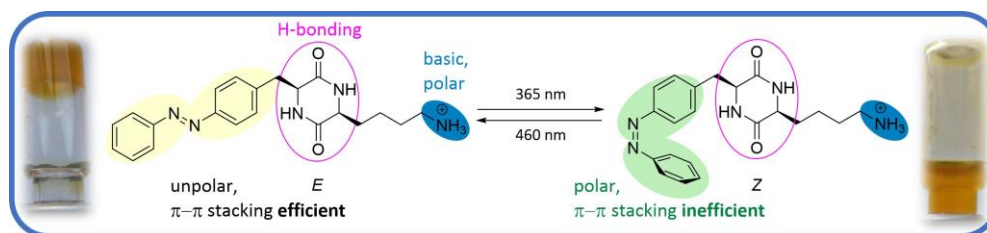


Figure 1: Photochromic hydrogel developed by Pianowski *et al.*; Based on this structural motif, further photochromic LMWGs were developed.^[5]

Here we present photochromic supramolecular hydrogels comprised of biocompatible low-MW cyclic dipeptide gelators with light-modulated polarity. They reversibly dissipate to fluids upon exposure on UV or visible light (for the non-halogenated and halogenated azobenzenes, respectively). They can encapsulate, and efficiently release upon irradiation a range of cargo molecules – oligonucleotides, proteins, antimicrobial, or anticancer agents. We discovered that tetra-*ortho* fluorinated azobenzenes (TFABs) – originally activated with green light – upon substitution with conjugated unsaturated substituents become sensitive to red light as well.^[6] Moreover, we developed a new method for stabilization of DKP-Lys-based hydrogelators by composite gelation of the basic cyclic dipeptide with polymeric acidic alginate.^[7]

Acknowledgements

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Combining SRFM and AFM techniques to investigate the inner structure of core shell microgels

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The role of microgels in various anticipated applications is well described in literature. [1] Their high variability in architecture and functionalities allows for modifying the polymeric network as well as accompanying properties. An important feature of microgels is their swelling behaviour, which highly depends on those modifications. However, many proposed applications depend on the diffusion of small molecules inside of a microgel. Quantification of this diffusion is a major challenge in microgel research. Single molecule tracking (SMT) approaches require single freely diffusing fluorophores inside a microgel which are tracked prior to leaving the polymeric structure. [2] One challenge here lies in the high number of fluorophores that typically accumulate inside microgels. Another challenge lies in the initial location. Fluorophores with initial locations in the microgel periphery can diffuse out of the microgel with relatively short tracks, thus reducing the accuracy and statistical impact of a measurement.

The presented work deals with the preparation of a core-shell microgel architecture that allows for implementation of fluorophores especially in the core. The overall system is supposed to represent a simple poly(N-isopropylmethacrylamide) (pNiPMAM) microgel, while in reality having a core that consists of pNiPMAM-co-N,N'-bis(acryloyl)cystamine (BAC) to immobilise fluorophores prior to SMT. The proposed release mechanism to initiate diffusion consists of DNA hybridisation and dehybridisation under controllable conditions. [3] Thus, the ideal technique to characterise the system is the super-resolved fluorescence microscopy (SRFM) technique of DNA point accumulation for imaging in nanoscale topography (PAINT). [2,4] Combined with the more general approaches of direct stochastic optical reconstruction microscopy (dSTORM) and Nile Red PAINT [2] as well as atomic force microscopy (AFM), we demonstrate the presence of further functionalities only in the core of the microgels. It is furthermore shown, in accordance to literature, that the core structure of a core shell microgel is an alteration of the simple microgel without shell. [5] This insight into the internal microgel structure may influence anticipated SMT measurements and expected results from those.

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**MODELING OF POINTS OF ENZYMATIC ACTIVITY OF
CHEMILUMINESCENCE ACTIVATED BY COUMARINS C-
314 AND C-334 UNDER THE ACTION OF CYTOCHROME C
COMPLEX WITH CARDIOLIPIN.**

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Chemiluminescence activated by natural dyes coumarins C-314 and C-334 has an intensity ~1500 and ~1600 times higher than spontaneous chemiluminescence of lipids, but at the same time does not differ from it in the parameters of kinetic curves and, accordingly, can be used to solve the problem of comparing the simulation of the number and magnitude of points of enzymatic activity of activated natural dyes coumarins C-314 and C-334 Chemiluminescence under the action of cytochrome C complex with cardiolipin.

The CytC-CL complex differs from the native CytC in the following properties: (1) it has the fluorescence of tyrosine and tryptophan residues; (2) it loses absorption in the Cope band (405-410 nm); (3) it has enzymatic activity and catalyzes the formation of lipid radicals in the membrane that trigger the chain process of lipid peroxidation. This process can be observed by chemiluminescence, both native and activated, as well as determine the number and magnitude of points of enzymatic activity.

In order to make a simulation of the magnitude and number of points of enzymatic activity, it should be taken into account that: (a) enzymatic activity depends both on the concentration of CytC and on the ratio determining the percentage of the absolute amount of denatured form; (b) the magnitude of the points of enzymatic activity was observed with the enhancement of chemiluminescence; (c) the mechanism of enhancement of chemiluminescence is energy transfer from the ketone molecule in the electronically excited state to the fluorescent level of the natural dye coumarin C-314 or the natural dye coumarin C-334.

Multi-responsive 4D Printed Bilayered Structures

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Employing 3D/4D printing for the fabrication of soft stimuli-responsive structures increases the variety of customized 3D shapes and paves the way towards potential applications in biomedicine and soft robotics. The term 4D printing refers to the ability of the 3D printed object to change its shape, size, or any other property upon stimulus/over time. An intensively studied stimuli-responsive motif is based on bilayers, i.e., combining a responsive active with a passive elastic layer, to induce bending deformation upon stimulus. Among different classes of 4D printable stimuli-responsive elastomers, liquid crystalline elastomers (LCEs) prove to be promising materials for a fast and highly reversible shape change upon switching from a nematic to an isotropic state. So far, 4D printing of macroscopic LCE structures is mainly explored with extrusion-based methods such as direct ink writing. Recently reported digital light processing (DLP) 4D printing of LCEs aimed to overcome existing limitations of extrusion-based techniques such as line-by-line printing and nozzle parameters limiting fabrication speed and resolution of the printed objects.

Herein, we explored the potential of entirely DLP 4D printed multi-material structures offering fully reversible bending actuation. For this purpose, we used DLP printed LCEs as active layers and combined it with a DLP printed elastomeric support acting as a passive layer. Furthermore, we were able to incorporate photoresponsiveness by embedding various light responsive moieties, e.g. organic dyes, in the LCE network following a simple post-modification protocol. In a detailed study, we showed the possibility to tune the bending of the bilayers upon the stimuli, temperature and light, by varying the LCE layer thickness. Our results were in good qualitative agreement with the theoretically expected trend. A highlight of our work was the observed wavelength-selective bending behavior of the fabricated bilayers with differently dyed LCEs. We demonstrated the potential of the observed selectivity in a gripper-like multi-material structure (**Figure**) which exhibited different bending patterns depending on the wavelength of the irradiation source.

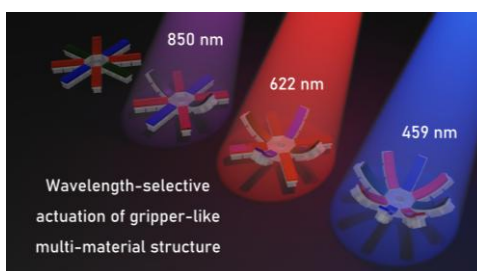


Figure: Fully DLP printed multi-material gripper-like structure with wavelength-selective bending.

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Unravelling the influence of environment-induced tuning on the photoisomerization reaction

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The ultrafast C=C double bond photoisomerization used in molecular motors and switches for optomechanical energy conversion at the molecular level, is hugely influenced by its environment like in the case of retinal in rhodopsin [1]. Applying a biomimetic approach, Tassone et al. [2] designed a light responsive protein composed of a synthetic chromophore - a xanthopsin derivative, mimic of the PYP chromophore – covalently bound inside the cavity of a model protein (hereafter called M2). This system is of great fundamental interest to investigate the influence of the environment (in particular steric hindrance and/or modification of the electrostatic interactions with the environment) on the chromophore photoisomerization.

We perform UV-Vis transient absorption spectroscopy of the chromophore (i) in solvents at different pH and (ii) encapsulated in the M2 protein, to explore the influence of the environment on the photoreaction dynamics and quantum yield (QY), in an attempt to unravel the physicochemical parameters that control the decay event at the conical intersection (CI).

It was clearly observed in solution, that in the anionic form there is a longer lived biexponential photoexcited state decay through the CI compared to its neutral form. Inside the M2 protein, the chromophore is in its neutral state, we are presently investigating the excited-state lifetime of the encapsulated chromophore (on going work).

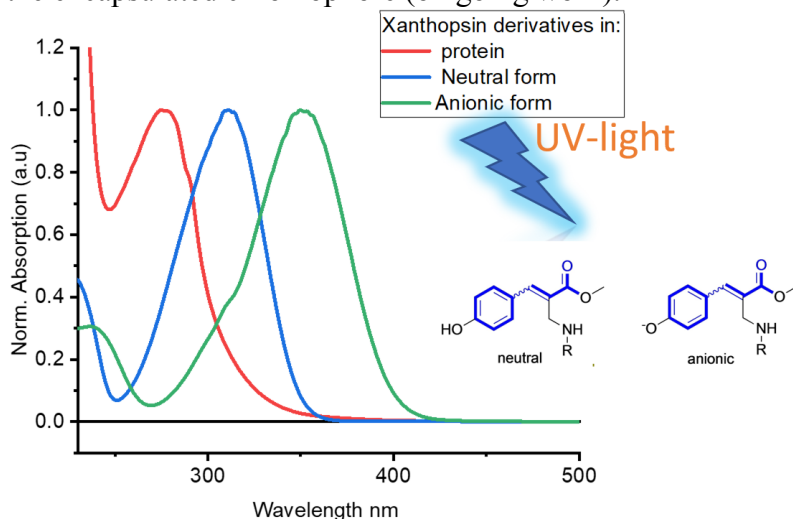


Figure 1: Xanthopsin like system, derivative of the PYP chromophore

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

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Localized surface plasmon-induced polymerization of free-radical acrylate monomers is an efficient, smart, and versatile method for preparing metal/polymer hybrid nanoparticles (NPs) with accurate control of the thickness and spatial distribution of the polymer on the NP surface. 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, through decay processes, the plasmon emitted light, hot charge carriers and heat, in less than tens of ns (Figure 1). If these processes are well-known, the main difficulty is to discriminate between them.

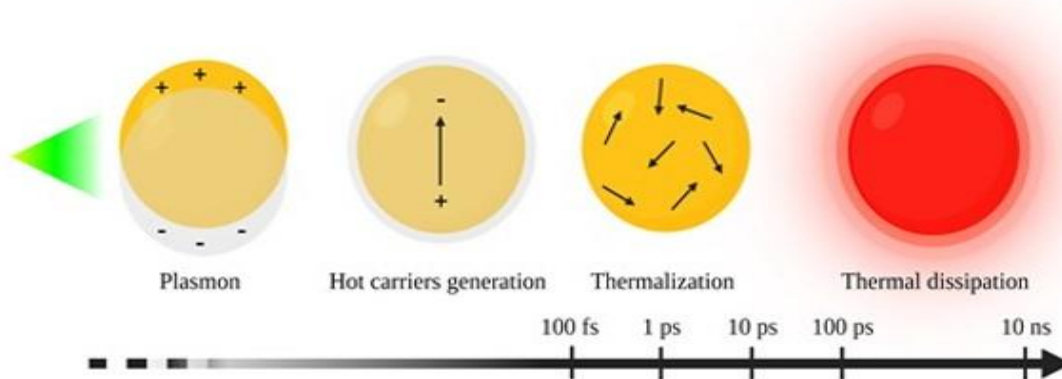


Figure 1: Plasmonic heat generation time-scale¹.

Previous experiments performed in the laboratory, highlighted the photochemical pathway as the main mechanism under mild irradiation². The thermoplasmonic pathway was already used to cure InZnO thin films³.

Here, we investigated thermoplasmonic to graft thermopolymer onto gold NPs. Different parameters were considered to address specifically thermopolymerization through the plasmonic excitation of NPs such as the NPs resonances, laser power and regime. Overall, to generate thermopolymerization through thermoplasmonic effect, high irradiation condition is required. Moreover, we observed thermopolymerization in ns-pulsed and continuous laser regime with different grafting features.

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Energy transfer and excited state chirality in an antenna complex emitting highly circularly polarised light

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Circularly-polarised luminescence (CPL) has promising applications in the fields of optical data storage, biomedical diagnosis and for the creation of more effective OLED displays. [1] Lanthanide-based chiral complexes have gained a lot of attention as CPL emitters due to their sharp and intense emission lines, long emission lifetimes and above all, due to their high degree of circular polarisation. Here, CsEu((+)-hfbc)₄ (hfbc = 3-heptafluoro-butylyrcamphorate) serves as the prototypical model compound displaying a record CPL emission, with 85% of the photons being left-circularly polarised at 595 nm (corresponding to a luminescence dissymmetry factor of 1.38). [2]

Although the luminescent transition is metal-centred (MC), the chiral ligands play a crucial role in the CPL phenomenon. First, they act as photosensitisers providing efficient energy transfer to the dipole-forbidden MC transition. Second, theoretical models predict that the high degree of luminescence dissymmetry arises from a transient coupling of ligand-centred electronic transition dipoles to the active MC transition of the europium ion, thereby creating a chiral luminescent excited state. [3,4] However, this CPL mechanism has not yet been captured experimentally, due to a lack of analytical techniques that combine chiral sensitivity with sufficiently high time resolution to capture the excited state dynamics.

Through a recently developed ultrafast polarisation spectroscopy technique with chiral sensitivity, we now present the first experimental investigation of both the ultrafast energy and transient chirality transfer to the luminescent excited state in CsEu((+)-hfbc)₄. [5] By covering the full spectral range from the visible to the deep ultraviolet, we are now able to determine the timescales of the relevant transfer processes and provide the first experimental analysis of the excited state CPL mechanism.

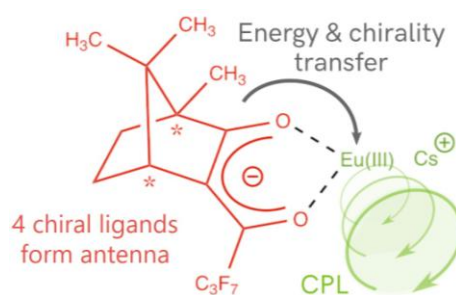


Figure 1: Energy and chirality transfer in CsEu((+)-hfbc)₄.

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Photoinitiation mechanisms of novel phenothiazine-based oxime and oxime esters acting as visible light sensitive Type I and multicomponent photoinitiators

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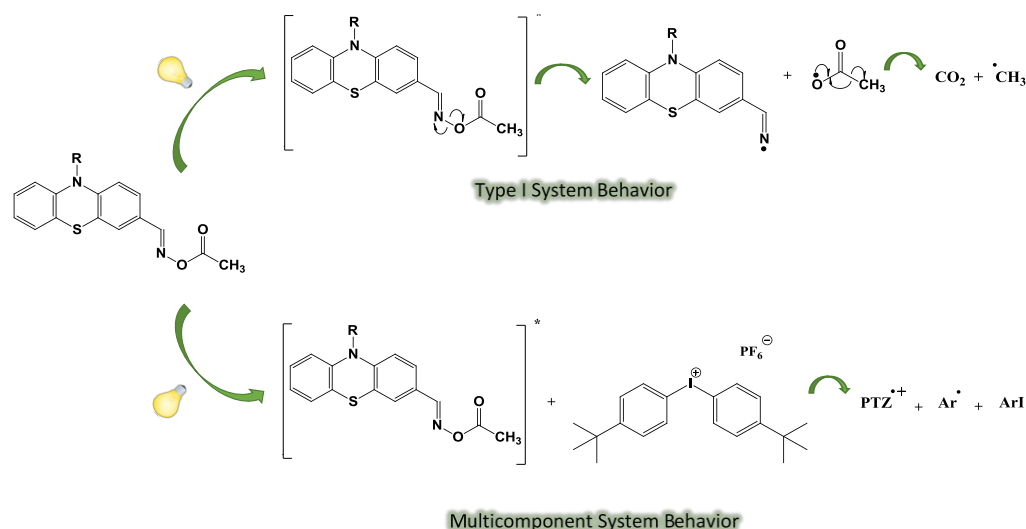
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In this work, three new photoinitiators, based on the phenothiazine scaffold as a chromophore and potentially bearing the oxime ester functionality as an initiating group were designed and synthesized for the free radical polymerization of acrylates, the cationic polymerization of epoxides, and the formation of interpenetrated polymer networks upon irradiation with a light emitting diode emitting at 405 nm. These phenothiazine-based oxime and oxime esters revealed impressive photoinitiation ability manifested by excellent polymerization rates and high final reactive function conversions. Significantly, they can be used as both; one-component (Type I) and two-component photoinitiating systems. Photoinitiation mechanisms through which reactive species are produced were investigated by means of different complementary techniques including real-time Fourier transform infrared spectroscopy, UV-visible absorption spectroscopy, electron spin resonance spectroscopy, fluorescence (steady state and time resolved), cyclic voltammetry, and molecular modelling calculations. Thermal initiation behavior of the different oxime esters was also studied by using differential scanning calorimetry, highlighting their dual thermal/photochemical initiation ability. Finally, 3D printed objects were successfully fabricated by conducting both direct laser write and 3D printing experiments.

Photoinitiation Mechanism



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Orthogonal switching in dual azobenzene photoswitches

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Molecules containing multiple photoswitches with orthogonal switching abilities are imperative for future advancements in applications of smart, multi-functional organic materials, e.g. in optical energy and information storage, or optical computing. Several challenges, such as energy loss channels via energy transfer or non-productive side reactions, must be overcome already by the initial design of the molecule to be a reasonable candidate for application.

A bis-azobenzene, consisting of a phenyl- and a hetero-azobenzene moiety, has been designed *a priori* using computational methods (TDDFT/CAM-B3LYP/6-311G*+D3(BJ)). Herein, *meta*-connectivity was applied for reduced π -conjugation between both moieties. The orthogonal switching behavior upon irradiation with different wavelengths was investigated and confirmed by ultrafast dynamics measurements and computational studies. These findings represent a significant progress towards finding new, efficient, and versatile organic multi-photoswitches, which can be utilized in smart materials, information storage, or molecular machines.

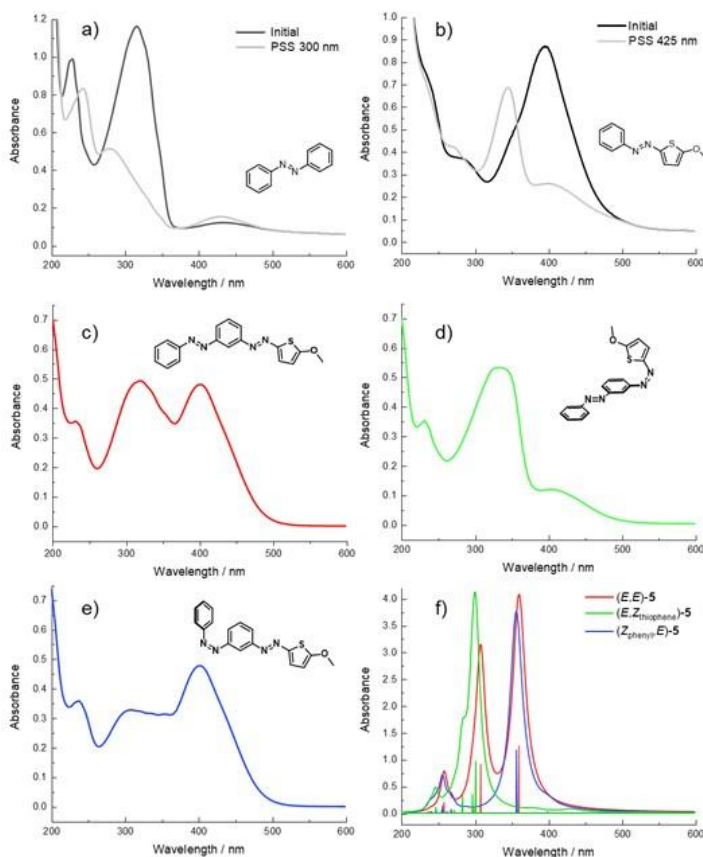


Figure 1: Experimental absorption spectra of the individual (a, b) and combined (c – e) photoswitches in their respective switching states implying, as well as the calculated absorption spectra (f) predicting, the orthogonal switching ability.

Targeted photodynamic therapy for cancer using Carbazole-BODIPY functionalized Graphene Oxide

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Nanotheranostic carriers are potent platforms for the treatment of cancer that present advantages over conventional agents for photodynamic therapy (PDT).¹ The unique properties of graphene oxide (GO) attracted much interest and studied for the potential applications in diagnostics and non-invasive therapy.²

Herein smart carbazole-BODIPY-glucose photosensitizer and/or chemotherapy drug Dox, were functionalized on GO via non-covalent method to obtain carbazole-BODIPY-GO and carbazole-BODIPY-GO-Dox nanoplatfoms for chemo-photodynamic dual therapy of cancer. The detailed characterization with fundamental photophysical and photochemical properties of such triplet photosensitizers and nanocarriers were studied. Carbazole-BODIPY dyad and related nanocomposites were studied to emcee efficient singlet oxygen generation upon light irradiation. We observed that the carbazole-BODIPY can be used as photocatalysts in the photooxidation of DPBF and the ¹O₂ photosensitizing abilities of the dyads and nanocarriers are greater than the conventional triplet sensitizer methylene blue. Also the interaction of target molecule and/or chemotherapy drug Dox with GO, nanoplatfoms containing Dox on the efficiency of singlet oxygen production and on the efficacies of the molecules in *in vitro* against K562 human chronic myelogenous leukemia cells were evaluated.

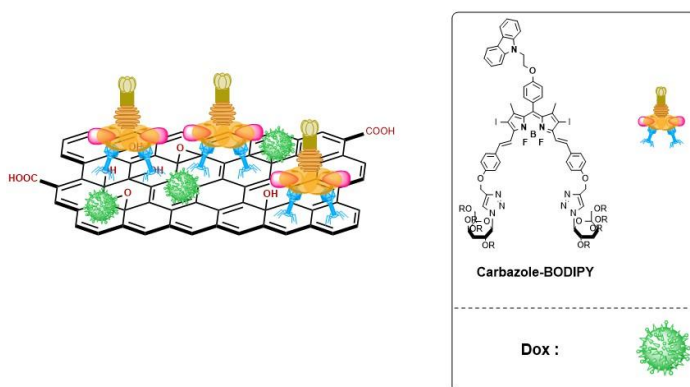


Figure : Schematic illustration of the carbazole-BODIPY-GO and carbazole-BODIPY-GO-Dox nanocarriers

Acknowledgements

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Highly fluorinated g-C₃N₄ for photocatalytic applications

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Graphitic carbon nitride (g-C₃N₄) has been investigated in the past years as an organic photocatalyst for potential application such as remediation (organics degradation), CO₂ artificial photosynthesis and for water splitting under light irradiation [1]. However, its applications are limited due to low utilization of the visible solar energy, low specific surface area and high recombination of photogenerated electron-hole pairs [2]. Therefore, carbonitride-based nanocomposites with engineered heterojunction and/or doping of g-C₃N₄ with elements such as B, C, N, O and F have been investigated. Few studies focused on the fluorination of g-C₃N₄ and with limited doping using mainly hydrothermal methods with F⁻ (*via* NH₄F or analogues) [3]. Recently, L. Sun *et al* have explored the F₂ (diluted) gas approach to prepare fluorinated g-C₃N₄ (F content of 7.05 at. %) with drastic structural distortion due to transformation of sp² hybridization carbon atoms to sp³ and enrichment of nitrogen defects [4]. It results with the improvement of absorption in the visible range and of the photocatalytic performance.

In order to extend the fluorination content and to investigate the resulting photocatalytic properties, carbonitride-base materials were fluorinated with pure F₂ gas at room temperature. The pristine materials were defective carbonitrides (CN and CNO) prepared from melamine decomposition and a g-C₃N₄ nanocomposites embedding carbon nanodomains (CCN) derived from the melamine/carboxylic adduct route [5]. The resulting highly fluorinated materials (F/C at ratio up to 0.96), after stabilization due to their explosive character, were characterized by a large panel of techniques such as X-Ray Diffraction, FTIR, XPS, diffuse reflectance spectroscopy (DRS), EPR in dark and visible mode and thermogravimetry analysis coupled with mass-spectroscopy (TG-MS). The photocatalytic properties of fluorinated materials were explored by studying the photodegradation kinetics of methyl orange using a Xe lamp. A significantly higher kinetics of degradation was observed for all fluorinated materials compared to their pristine counterpart.

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PHOTO-CONTROL OF G-QUADRUPLEX DNA FOLDING

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Guanine-rich sequences can self-assemble in stacked tetrads of guanines which are called G-quadruplexes. These secondary structures are highly polymorphic. Their folding and unfolding mechanisms have been shown to be involved in key cellular regulatory functions.¹ Hence, the photo-control of their folding processes is attracting a growing interest with applications in photo-pharmacology and DNA nanotechnology.² These processes can be induced by photoswitches such as cationic azobenzene derivatives like AZO1 (see figure below).^{3,4} I will present our work on the characterization of the interaction between such derivatives with different small G-quadruplex-forming DNA sequences using a variety of techniques including UV-visible spectroscopy, circular dichroism, NMR and femtosecond transient absorption.⁵ I will also present a time-resolved study by circular dichroism of the photoinduced folding/unfolding dynamics of these DNA complexes on the millisecond time scale.

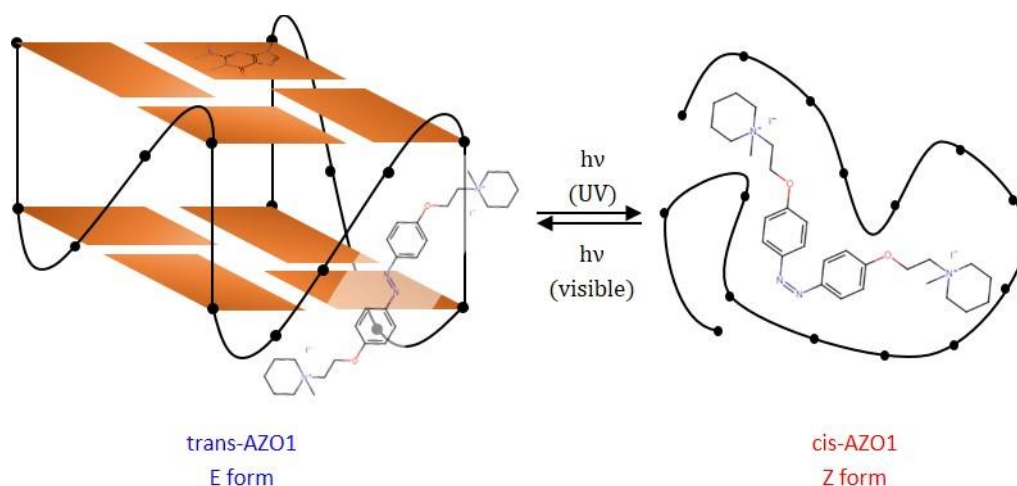


Figure : Schematic representation of the G-quadruplex – AZO1 complex before and after UV irradiation.

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Molecular Solar Thermal Energy Storage (MOST): Progressing from Molecular Design to a Functional Device

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Molecular Solar energy storage has been considered as a friendly way to harvest solar outcome. One major challenge in this context is the development of molecular solar fuels optimizing multiple properties, such as energy storage density, solar harvesting capacity, robustness, and heat release ability. Although various methodologies have been proposed to harness solar power, Molecular Solar Thermal (MOST)¹ technology has emerged as a promising candidate for sustainable and efficient solar energy capture and storage.

MOST relies on a photochemical transformation that converts a low-energy compound (a photoactive molecule) into a high-energy species configuration (a photoisomer), thereby storing energy in molecular bonds or metastable isomers. This stored energy can be released in the form of heat via a suitable catalytic process when needed.

In this contribution, we describe some of the main features that these systems must fulfil and our contributions in the MOST-EU project (H2020-FETPROACT-2019-951801), which aims to advance this technology towards a real application.²

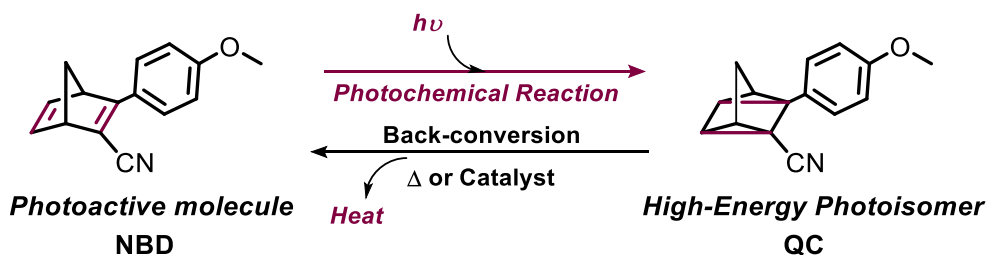


Figure 1: Norbornadiene-Quadracycline derivatives as MOST system.

Acknowledgements

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Hemipiperazine-Based Photochromic Sensors and Nanomaterials

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Stimuli-responsive materials constitute a rapidly developing field of research. They have found broad range of applications, for example in drug delivery systems^[1] or molecular machines.^[2] For precise control over the features of such materials, the incorporation of molecular photoswitches is particularly well suited, as light allows for non-invasive spatiotemporal tuning of their properties.

Our group has recently reported a novel class of molecular photoswitches based on cyclic dipeptides – hemipiperazines (HPI) – which photochromism is based on *E/Z*-photoisomerization of an arylidene substituent attached to a 2,5-diketopiperazine ring. Irradiation with specific wavelengths has been used to modulate cytotoxicity and fluorescence of these compounds.^[3] Based on these results, we have investigated further possible applications for these new photoswitches with the focus on smart materials. Here we report that certain HPI derivatives can be used as phototunable fluorogenic metal ion sensors, thereby combining a reversible response to light with a metal induced fluorescence increase. In a further step, it has been demonstrated that these complexes self-assemble into nanostructures, giving rise to complex multi-stimuli responsive systems.^[4] Our discovery paves the way to a new family of peptide-derived metal sensors and quantum confined materials. Future applications of HPI in other stimuli-responsive molecular architectures are feasible, i.a. due to extreme thermostability, robustness, and modular synthesis typical to the novel photochrome, as well as its compatibility with polar and aqueous environment.

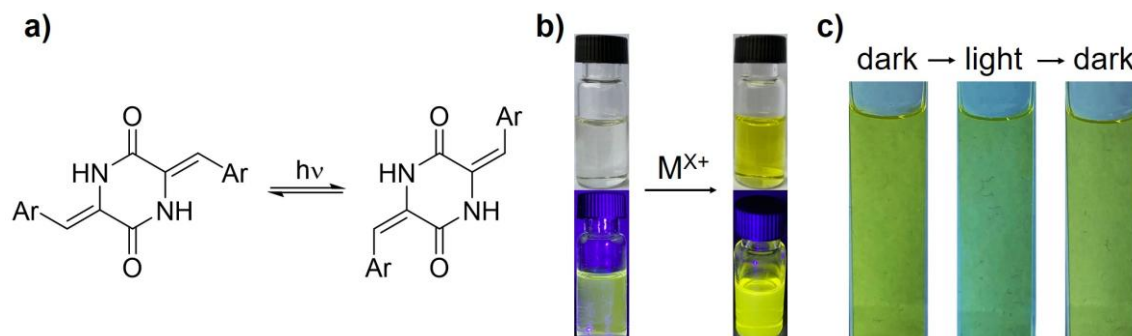


Figure 1: a) Core structure and photoisomerization of HPI photoswitches; b) change in color and fluorescence due to HPI-metal ion interaction; c) photochromism of a HPI-based complex.

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Photochemistry of Common Xanthene Fluorescent Dyes as photoCORMs

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Dyes are used in many areas of human activity, for coloring and visualization in various contexts. In (bio)medicine and research fluorescent dyes are often used as tags, reporters or diagnostic agents. Their degradation in environment proceeds either thermally, e.g. by hydrolysis, or photochemically.

We investigated the primary photoinduced chemistry of some of the most common such diagnostic dyes: fluorescein, eosin Y, and rose bengal; and major products of their photodegradation using a variety of techniques, e.g. optical spectroscopy, NMR, chromatography and mass spectroscopy. We found these substances, usually considered (photo)chemically stable, to liberate carbon monoxide (a bioactive gas with potential benefits) in 40–80% chemical yields upon extensive irradiation with visible light in aqueous solutions during their multistep concomitant degradation processes (Figure). In addition, other low-mass secondary photoproducts, such as phthalic and formic acids, were identified in the irradiated mixtures.¹ Using an experimental cell line model, we also demonstrated that these photochemical degradation pathways could have potential biological implications.²

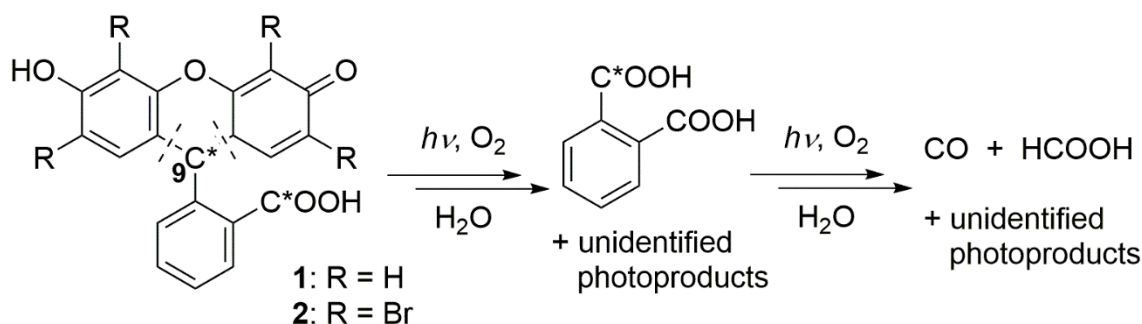


Figure: Multistep visible light induced photochemical degradation of xanthenes (fluorescein **1**, and eosin Y **2**) in aerated protic environment.

Acknowledgements

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Photomodulation of plinabulin – a tubulin polymerization inhibitor with low-nanomolar toxicity

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Photopharmacology has attracted growing interest in recent years. In this research area, molecular photoswitches are attached to bioactive agents to precisely control their activity both temporally and spatially. For example, the severe side effects of chemotherapy may be significantly reduced by local activation of a photomodulable drug in tumor tissue. However, modulation of the structure of a bioactive agent with a photoswitch often suffers from drastic reduction in its activity or biostability.

Plinabulin is a tubulin polymerization inhibitor with low-nanomolar activity^[1] that is in the third phase of clinical trials against non-small cell lung cancer (NSCLC) and chemotherapy-induced neutropenia (CIN)^[2]. We initially employed it as a dopant to study drug release experiments from photoswitchable hydrogels, but found that plinabulin itself is capable of photomodulation without further modification. The reason for this is that plinabulin contains a previously unexplored photoswitch motif in its structure, which we refer to as hemipiperazine (HPI). In contrast to other photopharmacological agents, plinabulin does not suffer from loss of activity due to structural changes and furthermore exhibits pronounced thermal stability and compatibility with aqueous media. In addition, the difference in toxicity between the two isomers is significant, being 85-fold (unidirectional) and 11-fold (bidirectional), respectively.^[3] Due to its many attractive properties, plinabulin represents a unique structure for the study and optimization of photomodulable bioactive agents.

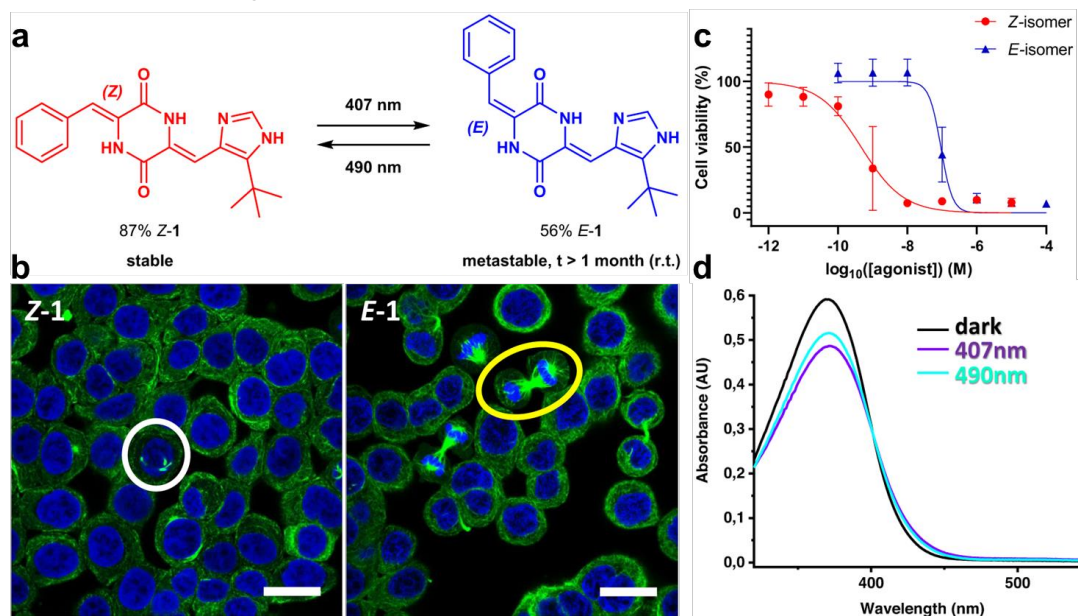


Figure 1: **a** The two photoisomers of plinabulin; **b** differences in the cytotoxicity of the isomers can be visualized via confocal microscopy and **c** quantified via MTT test; **d** UV-Vis spectra of plinabulin in the dark and at photostationary states.

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INVESTIGATION OF TWO-PHOTON POLYMERIZED MICROSTRUCTURES USING FLUORESCENCE LIFETIME MEASUREMENTS

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3D Microfabrication by two-photon polymerization (TPP) has become a very popular method to sculpt the matter at the microscale.^{1,2} One of the today's challenges is to exert a better control on the processing route and to achieve to build relationship between final properties of the material and the conditions of fabrication process. We report the use of fluorescence lifetime measurements for investigating two-photon polymerization (Figure 1).³ The dependency of the fluorescence lifetime of Bodipy-C12 with respect to its local environment was exploited to reveal heterogeneity in multi-material microstructures based on PETA and PEGDA-700. Furthermore, a correlation between writing conditions and local viscosity changes within polymerized microstructures made from PEGDA-700 was established by investigating the fluorescence lifetime changes of the molecular rotor. Based on these results, we anticipate that fluorescence lifetime measurement can be successfully applied to explore kinetics of two-photon polymerization or probe the 4D character of active 3D structures made by TPP.

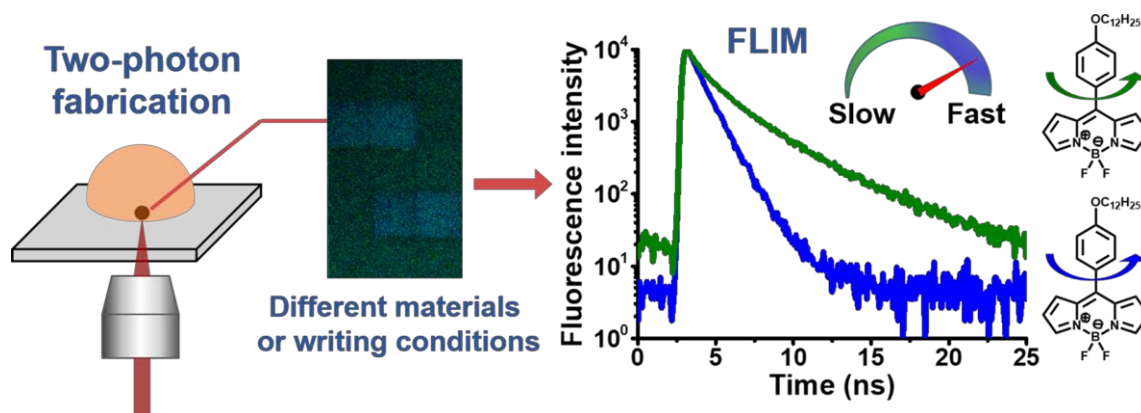


Figure 1 : Molecular rotor as viscosity probe to reveal heterogeneity in two-photon polymerized microstructures.

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CHITOSAN BIO-POLYMER AS A WATER-SOLUBLE RESIST FOR DEEP-UV (193 NM) PHOTOLITHOGRAPHY

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Conventional resists contain chemicals that may be hazardous to both human health and the environment. Skin irritation, breathing difficulties, and other health concerns might result from exposure to these substances¹. Also, the ecosystem may be at risk as rivers and soil may be contaminated by the dumping of toxic substances. We suggest a chitosan-based resist that performs with industrial equipment and allows for the creation of sub-micrometric patterns².

To further understand how chitosan and deep UV interact, various methods were applied. In particular, a comprehensive FTIR-ATR analysis was carried out, and the results of the EPR and SEC tests led to the establishment of a chitosan-DUV interaction mechanism³.

Moreover, methods for enhancing the resist's photosensitivity were investigated. The dose-to-clear can be reduced by two and four times, respectively, by adding a photosensitive chemical or altering the irradiation conditions.

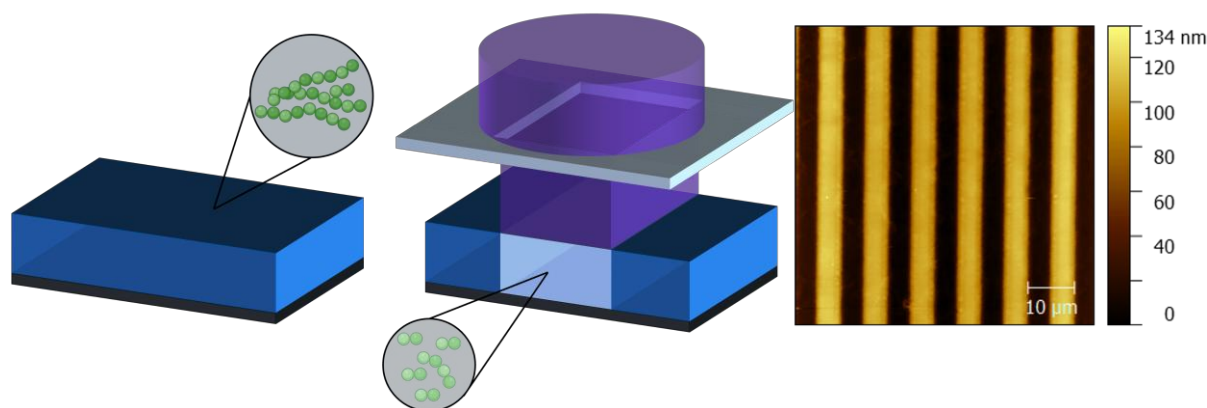


Figure: The schematic mechanism of photoinduced modification of chitosan photoresist with an example of obtained patterns.

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Computational Molecular Design of an Open-ring Azaacene Isomer

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N-heteropolycyclic aromatic compounds have been shown to be the most promising candidates for electron-transporting semiconductors. The molecular and spectroscopic features of N-heteropolycycles and open-shell radical and diradicaloid species are interesting to be investigated by theoretical computation at the electronic structure level. Through elaborate quantum chemical calculations, we will guide the synthesis and support the characterization of N-heteropolycyclic radicals and diradicals, and their spectroscopic features.

The ring-opening phenomenon while synthesizing a new tetraazahexacene derivative was observed only in the solid-state structure by our cooperation partners, the Bunz Group. However, in solution, the central ring remains closed in the azaacene derivatives. There are several possible strategies for designing an azaacene molecule which opens the central ring even in solution. Through DFT calculations performed with Q-Chem 5.2[1], we predicted which molecule remains with the ring open in solutions, e.g., DCM. Furthermore, once the target molecule is synthesized, the spectrum will be calculated and comparison between calculated and experimental spectrum will be helpful for the identification of the molecule.

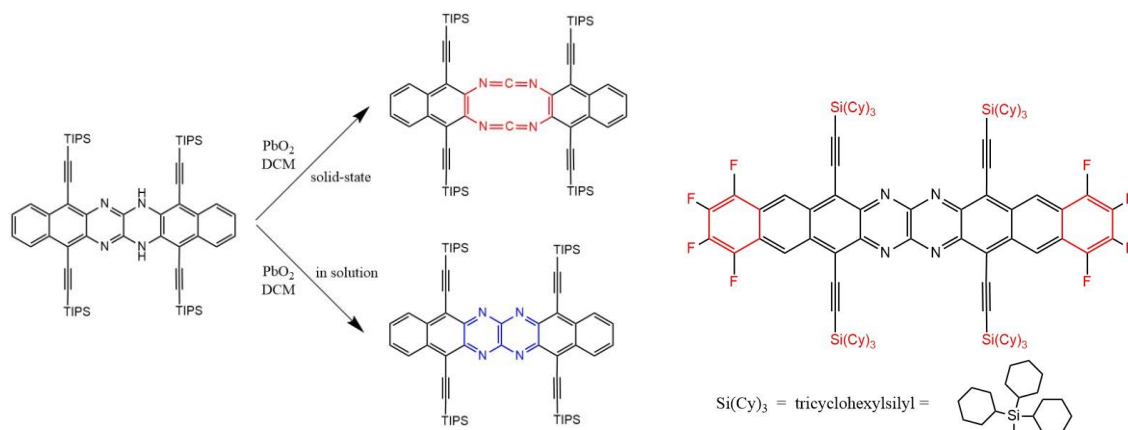


Figure: Left: the oxidation step where the ring opening was found;

Right: an example strategy predicted to obtain the stable open-ring isomer.

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Femtosecond spectroscopy of new iron bi-dentate complexes with extended lifetimes

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Within the scope of photocatalytic water splitting for green hydrogen production, iron-based complexes have been massively studied and optimized over the last ten years in order to reach the yield of their more efficient ruthenium counterparts^{1,2}. If the amount of iron in Earth's crust represents an undeniable asset compared to the one of ruthenium – making the latter not suitable for large-scale applications² – the lifetime of its triplet metal-to-ligand charge transfer (³MLCT) state remains its weakest spot, mostly because of its fast deactivation via the lower lying Metal Centered (MC) states¹. Increasing the ³MLCT lifetime of such iron-based light harvesters is therefore a real challenge that can be overcome thanks to a rational design of ligands³. In particular, Transient Absorption Spectroscopy (TAS) on newly developed Fe^{II} bi-dentate complexes with quinoline-based ligands revealed an interesting two-state parallel decay with an unprecedented lifetime of more than 100 ps. Clarifying the nature of the longer-lived excited state (³MLCT or ³MC) is then of central importance.

Assuming that only the ³MLCT state radiates, measurements with a streak camera have been carried out. An emission lifetime of more than 100 ps is indeed measured, but in addition to a nanosecond-scale signal, the origin of which (e.g. dissociated ligands) is still not understood.

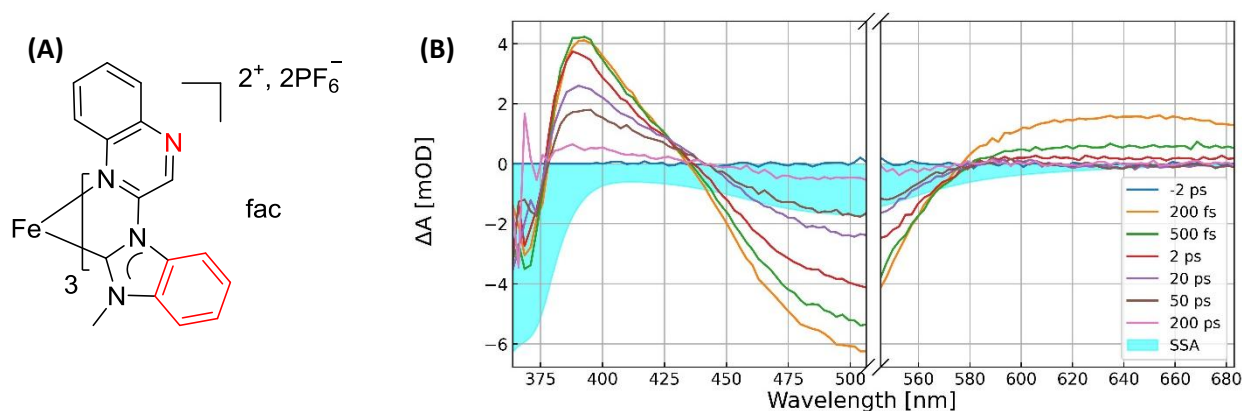


Figure 1. (A) Chemical structure of complex **366**. (B) Transient absorption spectra of complex **366**. The long-lived exc. state absorption (375-430 nm) and ground state bleach (450-570 nm) reveal an excited state with ≈ 130 ps lifetime.

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Development of novel photoinitiators for 3D laser nanoprinting

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The topic of 3D printing has become increasingly important in the last decades. The first print in three dimensions was carried out in the late 1980s in which 3D objects were constructed using computer-aided design software and printed layer by layer.^[1] 3D laser nanoprinting uses a laser beam to construct a structure in a medium. The printing materials used for this are resists consisting of a liquid monomer, which can be photopolymerized, and a photoinitiator that starts the polymerization chain by generating of radical.^[2]

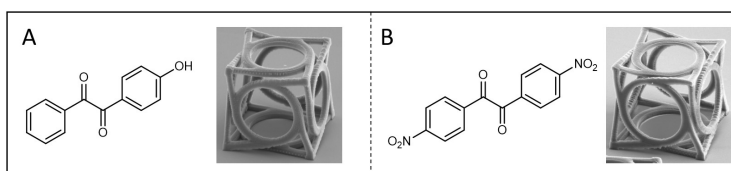


Figure 1: Selection of used 1,2-diketone based photoinitiator and their printed structures. A) 1-(4-Hydroxyphenyl)-2-phenylethane-1,2-dione printed with 240 μ W laser power; B) 4,4'-Dinitrobenzophenone printed with 229.5 μ W laser power

The underlying mechanism of these printing technique is the two-photon absorption. It is assumed that the light absorption of a single photon is insufficient to switch to an energetically excited state, whereas the simultaneous absorption of two photons can cause the photoinitiator to form radicals. Based on this theory firstly introduced by Marie Göppert-Mayer in 1931, Hahn *et. al.* developed the theory of two-step absorption.^[3,4] There are several requirements that the photoinitiator must fulfill for an application in two-step absorption 3D laser nanoprinting, 1,2-diketones, especially benzils, have been proven to be excellent photoinitiators. Herein, we report the synthesis and printing with a red (405 nm) and a blue (640 nm) laser of photoinitiators based on 1,2-diketones for applications in two-step absorption 3D laserprinting.

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Excited State Dynamics of Alkyl Substituted Perylene Derivatives in Highly Concentrated Solutions

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Symmetry breaking charge separation (SB-CS) allows for the conversion of solar energy into charge carriers by photoinduced electron transfer between identical molecules (M). In general, SB-CS is studied in systems in which the two chromophoric moieties undergoing SB are covalently linked, $M^*-M \rightarrow M^+-M^-$. Examples of bimolecular SB-CS, $M^* + M \rightarrow M^+ + M^-$, of organic chromophores yielding free ions, on the other hand, remain scarce due to solubility or aggregation issues of the dyes at high concentrations.

Recently¹, a new class of perylene (Pe) derivatives substituted with alkyl chains (R) in the 1-position (1-R-Pe) exhibiting an up to hundred times increased solubility in comparison to Pe in common organic solvents, have been synthesized. We investigated the excited state properties of these compounds at high concentrations using transient absorption (TA) spectroscopy in the visible domain whereby we observe self-quenching of the dyes as indicated by the rise of the Pe excimer² band, and a decreased excited state lifetime at higher concentrations (Fig. 1). Upon increasing the polarity of the solvent, the charge-transfer character of the excimer may be altered resulting in dissociation of the excimer into free ions.

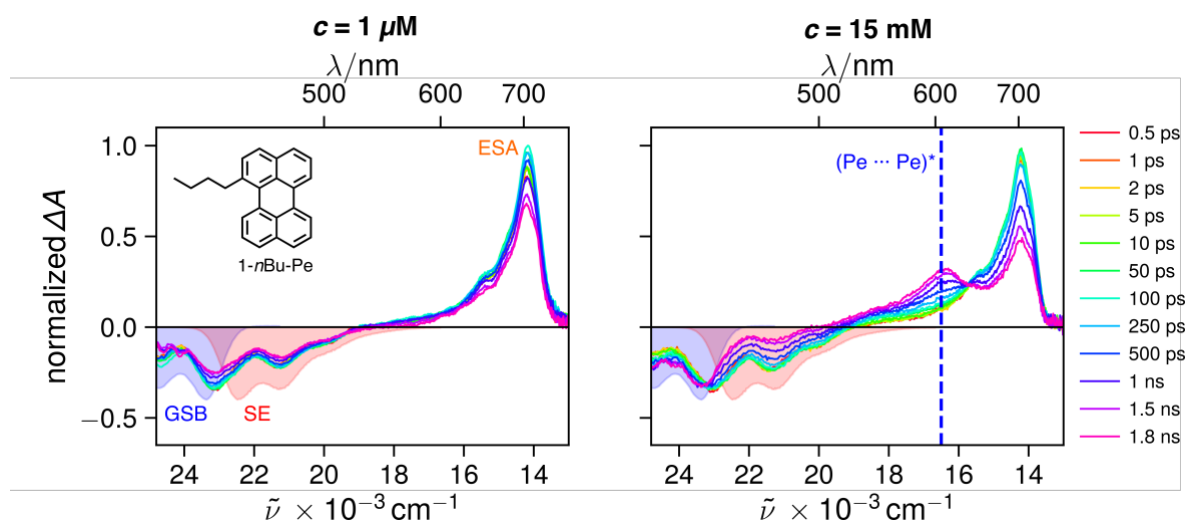


Figure 1: Femtosecond visible transient absorption spectra of 1-R-Pe (R = nBu) in acetonitrile at dilute (left) and concentrated (right) solution.

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Computational Investigation of Azaacene Diradicals and their Dimerization Reaction

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Open-shell molecules, such as diradicals and diradicaloids, exhibit interesting magnetic and electronic properties, making them attractive systems for both application and basic research. Areas of possible application include organic electronics, nonlinear optics and spintronics. From a quantum chemical perspective, they present a particular challenge since singlet diradicals cannot be correctly described by single-reference methods.

It was previously found that in isomeric quinoidal azaacenes the relative orientation of the sulfur atoms determines the diradical character. In this work, dicyanomethylene substituted benzodithienophenazines ***p*-1** and ***o*-1** (Figure 1a) are investigated regarding their diradical character, ground state multiplicity and optical properties using density functional theory (DFT) and (Spin-flip) time-dependent DFT (TDDFT). Furthermore, the unusual dimerization of the ortho-derivative forming four σ -bonds and resulting in a covalent azaacene cage is investigated using the semi-empirical tight binding method GFB2-xTB. The diradical character y_0 of ***o*-1** and ***p*-1** is determined to be 0.98 and 0.01 respectively. Spin-flip TDDFT calculations furthermore show that ***o*-1** has an open-shell singlet ground state with a singlet-triplet gap of 0.01 eV, while ***p*-1** has a closed-shell singlet ground state and a singlet-triplet gap of 1.30 eV. Investigation of the dimerization reaction suggests the consecutive formation of two sets of two σ -bonds as a plausible reaction mechanism. Electronic absorption spectra in solution are simulated using TDDFT for all compounds (Figure 1b).

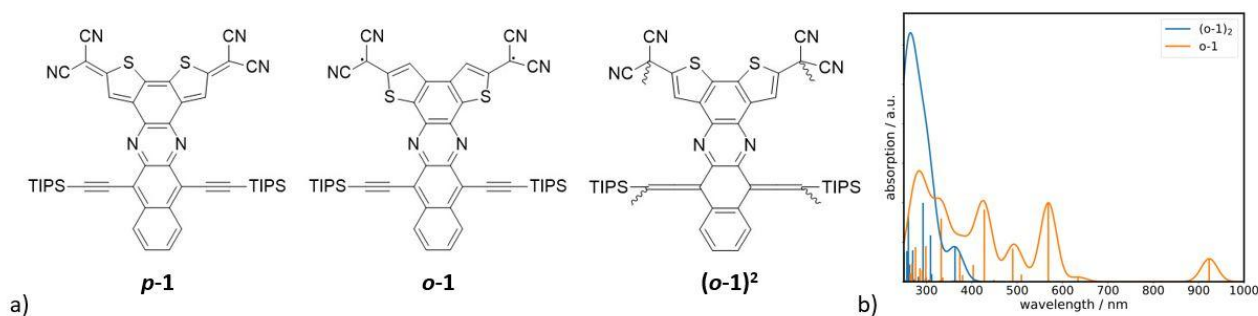


Figure 1: a) Chemical structures of dicyanomethylene substituted benzodithienophenazines ***p*-1**, ***o*-1** and dimerization product **(*o*-1)²**. b) Simulated UV-VIS-NIR spectra of **(*o*-1)²** and ***o*-1** in *o*-dichlorobenzene (wB97X-D3/def2-svp, C-PCM, $\epsilon_0=9.93$).

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Effects of the Solvents and Oriented External Electric Field on the Tautomerism of 7-Hydroxyquinoline

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7-hydroxyquinoline (7OHQ) is an interesting example of a long-range proton transfer. Due to the large distance between the oxygen and nitrogen atoms, the excited state proton transfer is either solvent or concentration assisted [1]. In the present work, the solvent assisted excited-state intermolecular proton transfer process has been investigated in methanol and in presence of water by using steady state spectroscopy. An equilibrium between the enol and keto tautomers in 7OHQ is detected after analyzing the absorption and emission spectra. The enol form is much more stable in the ground state, while the keto form is much more polar. This gives an additional opportunity to mimic the solvent effect by applying an oriented external electric field (OEEF).

After a thorough literature analysis regarding the influence of the OEEF over equilibrium systems [2], we have constructed a specific experimental set-up, which allows us to simultaneously investigate the absorption and fluorescence spectra of molecular solutions under the influence of an OEEF.

We believe that such technique, which could give us more information about the selective stabilization of a given tautomer, could have interesting applications in any kind of equilibrium processes.

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PHOTOSWITCHABLE NANOPARTICLES AS POTENTIAL HIGH-CONTRAST PHOTOACOUSTIC AGENTS

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Photoacoustic (PA) imaging is an emerging and non-invasive molecular imaging technique that combines optics and ultrasounds.¹ Specifically, acoustic waves are generated in response to light excitation of chromophores, providing high-resolution images of the optical marker distribution. This versatile bioimaging technique has shown the potential to follow up biological processes in immune cells, like inflammation, cardiovascular disfunction and stroke.² However, a high density of absorbing molecules is usually required. In order to overcome this limitation, organic nanoparticles, comprising a high payload of dyes, have appeared as a promising alternative to molecular dyes in solution.³ Yet, the need for high photostability and non-radiative relaxation after excitation prompted us to focus our interest on photochromic compounds, undergoing significant geometry and vibrational motions in the excited state. With this aim in mind, we have synthesized azo compounds, amenable to switch between two stable isomers with high E→Z and Z→E conversion yields (> 80 %) using green (540 nm) and UV or blue light. In order to avoid disassembling of the nanoparticles, issued from dye self-assembling in water, cross-linked architectures have been targeted. Photochromism of the azo dyes has been performed with dyes in solution or processed as nanoparticles. In addition, photoinduced geometrical changes of the nanoparticles have been followed at the nanoscale using dynamic light scattering (DLS) and atomic force microscopy (AFM). As a prospect, combined photochromic and photoacoustic investigations need to be performed to assess the impact of each photoreaction on the generation of acoustic waves.

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