PhotOnline'2023

*SP$_2$P web-conference organized **by** and **for** young researchers – 2nd edition*

1-2
February
2023

Gather

Programme and book of abstracts

Words of the SP2P President

Dear participants,

The organizing committee of "PhotOnline" is pleased to welcome you for this web conference, which will be held on February 1 and 2, 2023 on the Gather platform.

This web conference is organized under the auspices of the Photochemistry, Photophysics and Photosciences (SP2P) of the Chemistry-Physics Division (French Chemical Society / French Physical Society). This is the second edition of "PhotOnline", organized by and for the young photochemists of SP2P.

The first edition was organized in the context of the Covid crisis and the cancellation of a large number of scientific events. Fortunately, we are out of this turbulent context but in consultation with the young researchers of SP2P, we have decided to maintain this event which gives an opportunity to young researchers (PhD students, post-docs, students in training, young permanent staff...) to find a forum to present their results. This conference completes the annual scientific days that will be held in May this year and it is of course open to "less young" researchers, professors and experienced engineers who can share their knowledge, ideas and advice.

It is also an opportunity for young photochemists to have a first experience of organizing a conference, to get involved, to dynamize and to federate. You will quickly realize the great work they have done to set up this conference.

As you will discover in this document, this edition is open to the international, with 11 different nationalities and communications that will be given from Italy, Spain, Portugal, Belgium, Russia, Nigeria ... I would like to take this opportunity to warmly thank our colleagues abroad who have spread the word about these days.

Another novelty for this edition: the use of the Gather platform which allows to propose you a more convivial environment and favorable to the scientific exchanges.

The program of these two days is really attractive, with 4 invited conferences (Prof. Karl Börjesson, Prof. Serena Silvi, Dr. Adèle Laurent, Prof. Peter Dedecker), 33 oral communications, flash communications and posters. Prizes for the best presentations will be awarded at the end of the day, thanks to the support of our sponsors.

We look forward to meeting you at "PhotOnline" on February 1 and 2 and hope that you will all enjoy discovering and sharing your findings, theories and ideas in a relaxed and friendly atmosphere.

Olivier Soppera

President of SP2P

Words of the organizing committee

It is our great pleasure and privilege to organize the second edition of the PhotOnline. This event is an opportunity for all young researchers to exchange about their exciting scientific achievements and to create a scientific & human network under a pleasant atmosphere.

We organized a program covering various topics and performances presented by French and international speakers. You will have the possibility to attend four keynote presentations, 33 oral communications, 20 flash presentations, and 9 poster presentations.

We want to thank the invited speakers warmly: Prof. Karl Börjesson, Prof. Serena SILVI, Dr. Adèle LAURENT, and Prof. Peter DEDECKER. We wish to express our gratitude for accepting our invitation.

We also thank SP2P office members who entrusted us with this conference organization, being at the same time supportive and ready to help, but also giving us total freedom in decision making.

Needless to say, this event is only possible with our kind sponsors. We want to express our gratitude to École Doctorale PCP, HiFunMat, Institut de Science des Matériaux de Mulhouse, Institut des Sciences Moléculaires Bordeaux, MatLight, QMat, Réseau des Jeunes Chimistes Société Chimique de France, Société Chimique de France Section Alsace, and Université de Haute-Alsace.

And last but not least, we thank every participant at this conference. We sincerely hope these two days will be instructive and rich in encounters for all of you! We wish you an enjoyable attending!

The organization committee PhotOnline 2023

The organizing committee

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Planning

Planning (Paris time zone UTC +1)

Wednesday, February 1, 2023

09:00 – 9:20	Welcoming speech

9:20 – 10:00	**Prof. Karl BÖRJESSON** - Strong exciton-photon coupling using organic molecules

10:00 – 12:15	Photophysical and photochemical processes: chemical transformations, photochromism, fluorescence, electron and energy transfer

OC01 ➢ 10:00 - **Benjamin MOUROT** – Coupling principe: Towards of new family of NIR absorbing dyes.

OC02 ➢ 10:15 - **Kais DHBAIBI** – Pathways to improve the chiroptical properties of helicene molecules via exciton coupling chirality.

OC03 ➢ 10:30 - **Nil SANOSA I FERRO** - Hydrogen Atom Transfer: a powerful strategy for accessing α-amino ketyl radicals.

10:45 –11:00	Coffee break

OC04 ➢ 11:00 - **Yang ZHOU** - Competitive Photoisomerization and Energy Transfer Processes in Fluorescent Multichromophoric Systems

OC05 ➢ 11:15 - **Maria João ÁLVARO ALBUQUERQUE MARTINS** - Light-responsive quinoline-foldamers with photo-switchable On/Off conductivity.

OC06 ➢ 11:30 - **Bassima HOTEIT** - Synthesis and Characterization of Photo-activatable Systems.

OC07 ➢ 11:45 - **Mariia HRUZD** – Tunable phosphorescence via the structure design of cyclometalated Pt(II) complexes.

OC08 ➢ 12:00 - **Zhaoxin WANG** - Synthesis of azobenzene-based saccharides and investigation of their photoswitching properties in water.

12:15 – 13:20	Lunch

13:20 – 14:00	**Prof. Serena SILVI** - Photoactive molecular devices and machines

14:00 –14: 45	Techniques for studying photoinduced reactions: spectroscopies, microscopi modeling

OC09 ➢ 14:00 - **Thomas AUBINEAU** - Design, characterization and evaluation of a lab-made photoreactor: a first step towards standardized procedures in photocatalysis.

Planning (Paris time zone UTC +1)

OC10
- 14:15- **Saül GARCIA-ORRIT** - Symmetry drives fused nanographene-metalloporphyrin conjugates photophysics.

OC11
- 14:30 - **Orlando VILLEGAS** - Mechanical effect produced by photoswitchable reactions: insights from molecular simulations.

14:45 – 15:25	Flashs – Flashs presentations

15:25 – 16:25	Poster and coffee break

16:25 – 16:40	Photophysical and photochemical processes: chemical transformations, photochromism, fluorescence, electron and energy transfer

OC12
- 16:25 - **Stephania ABDALLAH** - Two-Photon Active o-Carborane Branched Initiators for 3D-Microfabrication of Thermo-Switchable Fluorescent Materials devoted to Optical Data Storage.

16:40 – 17:55	Applications: nanotechnologies, nanomaterials, natural and artificial photosynthesis, photovoltaics, molecular electronics, photocatalysis, organic photochemistry, sensors

OC13
- 16:40 - **Erbiai El Hadi** - Investigation of the Superoxide Anion Sensing Potential of Brominated Coelenterazine Analogs.

OC14
- 16:55 - **Diana CRISTA** - Evaluation of pH and stoichiometry of the n-dopant effect into carbon dots properties.

OC15
- 17:10 - **Pablo JIMENEZ-CALVO** - Sulfur-doped carbon nitride hybrid materials tested under green light for photoelectrocatalytic benzylamine oxidation and oxygen evolution reactions.

17:25 – 17:55	Photophysical and photochemical processes: chemical transformations, photochromism, fluorescence, electron and energy transfer

OC16
- 17:25 - **Aoudjit THINHINANE** - Photochemical imaging of near-field and dissymmetry factor in chiral nanostructures.

OC17
- 17:40 - **Rana MHANNA**- Geometry-driven mass transport dynamics within permeable 3D—microstructures fabricated by two-photon polymerization with Y-shaped triphénylamines initiators.

Planning (Paris time zone UTC +1)

Thursday, February 2, 2023

09:00 – 9:40 **Dr. Adèle Laurent** - Light on photoactive molecules through theoretical chemistry

9:40 – 10:00 A word from sponsors

10:00 – 10:45 Photophysical and photochemical processes: chemical transformations, photochromism, fluorescence, electron and energy transfer

OC18 ➢ 10:00 - **Yoann OLIVIER** - Insights from computational modeling on the singlet-triplet conversion in MR-TADF and invert singlet-triplet gap materials.

OC19 ➢ 10:15 - **Houda MOUMENE** - QM/MM calculations and spectra modelling of the bioluminescent system Nanoluc-Furimamide.

OC20 ➢ 10:30 - **Josene TOLDO** - Molecular light-to-heat converters: a new strategy for an old problem.

10:45 – 11:00 Coffee break

11:00 –12:00 Materials prepared by photochemical processes and/or photoactivatable materials: photoactive supramolecular systems, photopolymers

OC21 ➢ 11:00 - **Francesca LANERI** - A Supramolecular Nanoassembly of Lenvatinib and a Green Light-Activatable NO Releaser for Combined Chemo-Phototherapy.

OC22 ➢ 11:15 - **Ainhoa OLIDEN** - Tuning the Photophysics of ITQ-51 Zeotypic Structure.

OC23 ➢ 11:30 - **Constance THOMAS** - Resin Additive for UV 3D printing resins with (Bio)degradable properties.

OC24 ➢ 11:45 - **Antonio FIORENTINO** - Guest release from liposomes using visible light.

12:00 – 13:05 Lunch

13:05 – 13:45 **Prof. Peter DEDECKER** – More informative imaging using ‘smart’ labels and novel instrumentation

13:45 – 14:15 Materials prepared by photochemical processes and/or photoactivatable materials: photoactive supramolecular systems, photopolymers

Planning (Paris time zone UTC +1)

OC25 ➢ 13:45 - **Ruth PRIETO-MONTERO** - Clay-based and mesoporous silica nanoparticles as carriers for photodynamic therapy.

OC26 ➢ 14:00 - **Auriane PERRIN** - Photo-control of G-quadruplex DNA folding.

14:15 – 14:30	Photophysical and photochemical processes: chemical transformations, photochromism, fluorescence, electron and energy transfer

OC27 ➢ 14:15 - **Lazare SALADIN** - BrightSwitch®: A New Family of Dual Emissive Photoconvertible Fluorescent Probes for Bioimaging.

14:30 – 14:45	Applications: nanotechnologies, nanomaterials, natural and artificial photosynthesis, photovoltaics, molecular electronics, photocatalysis, organic photochemistry, sensors

OC28 ➢ 14:30 - **Cristina PARISI** - A novel molecular dyad for combined PDT and NO-PDT in cancer cells

14:45 – 15:00	Coffee break

15:00 – 16:15	Flash presentations

16:15 – 17:30	Photophysical and photochemical processes: chemical transformations, photochromism, fluorescence, electron and energy transfer

OC29 ➢ 16:15 - **Leonardo ANDREONI** - A Multiresponsive Calix[6]arene Pseudorotaxane Empowered by Fluorophoric Dansyl Groups.

OC30 ➢ 16:30 - **SILVA José** - Development of Superoxide Anion Sensing Compounds based on Chemiluminescent Coelenterazine.

OC31 ➢ 16:45 - **Tatiana MUNTEANU** - From natural chromophores to organic dyes: exploring the chemistry of c- and n-substituted phenazines.

OC32 ➢ 17:00 - **Valentina FERRARO** - Luminescent Tetrahedral and Octahedral Manganese(II) Complexes with [O=P]-donor Ligands.

OC33 ➢ 17:15 - **Marius HERVE** - Non-reversible Photoinduced Phase Transition in the RbMnFe Prussian Blue Analogue Studied by Streaming Crystallography.

17:30 – 18:00	Coffee break

18:00 – 18:20	Awards and closing ceremony

Invited speakers

INVITED SPEAKER 1

Pr Karl BORJËSSON - *Univ. of Gothenburg*

Strong exciton-photon coupling using organic molecules

Strong light-matter coupling generates hybrid states that inherit properties of both light and matter, effectively allowing the modification of the molecular potential energy landscape. This phenomenon opens up a plethora of options for manipulating the properties of molecules, with a broad range of applications in physics, chemistry, and materials science. In this presentation, I will discuss how the relaxation between hybrid light-matter states and molecular centered states can be used in molecular systems. Specifically on the possibility to modify energetic driving forces and to efficiently harvest excitation energy in planar heterojunctions by utilizing the delocalized nature of hybrid light-matter states will be discussed.

References:

General strong exciton-photon coupling
Hertzog, Wang, Mony and Börjesson
Strong light–matter interactions: a new directionwithin chemistry
Chemical Society Reviews, 2019, 48, 937-961.

On the interplay between molecular centered states and polaritons
Ye, Mallick, Hertzog, Kowalewski and Börjesson
Direct Transition from Triplet Excitons to Hybrid Light–Matter States via Triplet–Triplet Annihilation
Journal of the American Chemical Society, 2021, 143, 19, 7501-7508.

Yu, Mallick, Wang and Börjesson
Barrier-free reverse-intersystem crossing in organic molecules by strong light-matter coupling
Nature Communications, 2021, 12, 3255.

Mony, Climent, Petersen, Moth-Poulsen, Feist and Börjesson
Photoisomerization Efficiency of a Solar Thermal Fuel in the Strong Coupling Regime
Advanced Functional Materials, 2021, 31, 2010737.

Wang, Hertzog and Börjesson
Polariton-assisted excitation energy channeling in organic heterojunctions
Nature Communications, 2021, 12, 1874.

Stranius, Hertzog and Börjesson
Selective manipulation of electronically excited states through strong light–matter interactions
Nature Communications, 2018, 9:2273.

INVITED SPEAKER 2

Pr Serena SILVI - *Univ. of Bologna*

Photoactive molecular devices and machines

Molecular machines and motors are assemblies of a discrete number of molecular components, designed to be set in motion relative to one another. (Pseudo)rotaxane architectures are based on interlocked structures, wherein a macrocyclic component encircles and shuttles along an axle like molecule. By appropriate design, the assembly of the molecular components, as well as their relative motion, can be controlled by application of an external stimulus. Light is the most valuable energy source to operate a molecular device, because it can be controlled in terms of space, time and energy, it is clean, and it can be used both to "read" and "write" the state of the system.

A common strategy for the operation of molecular devices relies on the use of photochromic compounds, either in combination with or integrated within the molecular machine. Indeed, the structural rearrangement associated with the photoisomerization reaction can be accompanied by the emergence of new properties (e.g., acid-base properties), an alteration of the electronic distribution and a structural rearrangement of the photochromic compound. These transformations can be exploited to operate the molecular machine, by modulating the extent of the interactions between the molecular components and/or the kinetics of the molecular motions.

INVITED SPEAKER 3

Dr Adèle LAURENT – University of Nantes

Light on photoactive molecules through theoretical chemistry

Adèle D. Laurent (born in 1985) received her PhD in 2010 from the *Université de Lorraine* (Nancy, France). Next she spent two months at the Polytechnic University of Catalonia (Prof. Aleman) before moving to the University of Southern California for a post-doctoral stay (Prof. Krylov). In October 2012 she obtained a permanent CNRS researcher position at the *Nantes Université*. As computational chemist, she works on the theoretical simulations of the optical properties of dyes[1] and of photochromes.[2] Since long time, she is also keen on biological systems studying ligand-protein or protein-protein interactions in order to determine new potent inhibitors.[3] Taken together, she combined her expertize in quantum mechanics (QM) and molecular mechanics (MM) to focus on the modelling of photoprocesses in condensed phase and in fluorescent biomolecules.[4]

References:

[1] (a) A. D. Laurent and D. Jacquemin* *Int. J. Quant. Chem.*, 113, 2019 (2013). (b) A. D. Laurent, C. Adamo and D. Jacquemin* *Phys. Chem. Chem. Phys.* **16**, 14334 (2014). (c) Y. Houari, S. Chibani, D. Jacquemin and A. D. Laurent* *J. Phys. Chem. B* **119**, 2180 (2015). (d) T. Pariat, T. Stoerkler, C. Diguet, A. D. Laurent,* D Jacquemin,* G. Ulrich,* J. Massue* *J. Org. Chem.* **86**, 1760 (2021),

[2] (a) M. Di Donato, M. M. Lerch, A. Lapini, A. D. Laurent, A. Iagatti, L. Bussotti, S. P. Ihrig, M. Medved, D. Jacquemin, W. Szymanski, W. J. Buma, P. Foggi, B. L. Feringa* *J. Am. Chem. Soc.* 139, 15596 (2017). (b) M. W. H. Hoorens, M. Medved, A. D. Laurent, M. Di Donato, S. Fanetti, L. Slappendel, M. Hilbers, B. L. Feringa,* W. J. Buma,* W. Szymanski* *Nat. Commun.* **10**, 2390 (2019).

[3] (a) T. Jaunet-Lahary, Daniel P. Vercauteren, F. Fleury, A. D. Laurent* *Phys. Chem. Chem. Phys.* 20, 18020 (2018). (b) N. Tripathi,* L.Leherte, D.V. Vercauteren, A.D. Laurent* *J. Comput. Aided Mol. Des.* **35** 337 (2021). (c) N. Tripathi, R. Danger, M. Chesneau, S. Brouard, A. D. Laurent* *J. Mol. Graph. Model.* **114**, 108167 (2022).

[4] (a) S. Budzák, A. D. Laurent, C. Laurence, M. Medved and D. Jacquemin* *J. Chem. Theory Comput.* **12**, 1919 (2016). (b) M. Asad, and A. D. Laurent* *Phys. Chem. Chem. Phys.* **24**, 3816 (2022).

INVITED SPEAKER 4

Pr Peter DEDECKER – *KU Leuven*

More informative imaging using “smart” labels and novel instrumentation

Biography

Peter Dedecker received his Ph.D. in Chemistry from the KU Leuven, Belgium, in the group of Johan Hofkens. He then spent 6 years as a postdoc in the Hofkens group and the group of Jin Zhang, then at the Johns Hopkins University School of Medicine, Baltimore, MD, before returning to the KU Leuven as an assistant professor. Over his career, he has worked in various fields, including spectroscopy, optics, biochemistry, and imaging. Since 2015 he has been the head of the Lab for Nanobiology at KU Leuven, where his research focuses on developing strategies, fluorophores, and instruments for the visualization of spatiotemporal heterogeneity in cellular processes.

PhotOnline'2023

Oral Communications

OC 01

Coupled Polymethines: Towards a new family of NIR absorbing dyes

Benjamin Mourot,*[1] Rudraditya Sarkar,[2] Valérie Mazan,[3] Mourad Elhabiri,[3]
Denis Jacquemin,[2] Olivier Siri,[1] Simon Pascal[1]

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Keywords: Polymethines, Coupling Principle, Coupled Polymethines, Acidochromic dyes, Acidoswitches.

Polymethine dyes, often referred to cyanines, are organic chromophores with an even number of π electrons delocalized between two terminal heteroatoms over an odd number of unsaturated carbon atoms. Upon molecular engineering (extremities, conjugation length…), polymethines are capable of absorbing up to the nearinfrared (NIR) region and are therefore used in multiple applications ranging from molecular electronics[1a] to bioimaging [1b] and nonlinear optics.[1c]

According to a theoretical study by Dähne and Leupold published in 1966, the coupling of two polymethines subunits linked by two sigma bonds would induce an enhancement of optical properties.[2] So far, dyes introducing multiple polymethine subunits have been scarcely reported, the most recent examples being redabsorbing zwitterions based on benzoquinone monoimine (BQMI)[3a] and diaminobenzoquinone diimine (DABQDI).[3b]

With the aim to use the coupling strategy to develop new families of dyes, we recently synthesized coupled polymethines incorporating anionic oxonol and cationic heptamethine subunits that gave rise to unprecedented derivatives holding potential as pH- and photo-switches, providing a wide span of absorption up to the NIR domain.

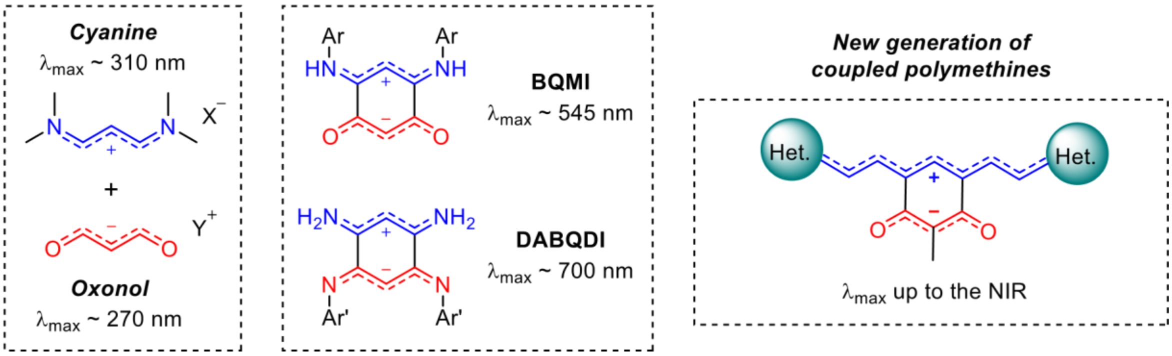

Figure 1. Examples of respectively : trimethines, coupled trimethines and new generation of coupled trimethine and heptamethine.

[1] a) D. Saccone, S. Galliano, N. Barbero, P. Quagliotto, G. Viscardi, C. Barolo, *Eur. J. Org. Chem.* **2016.(13)**, 2244 (2016); b) W. Sun, S. Guo, C. Hu, J. Fan, X. Peng, *Chem. Rev.* **116.(14)**, 7768 (2016); c) S. Pascal, S. David, C. Andraud, O. Maury, *Chem. Soc. Rev.* **50.(11)**, 6613 (2021).

[2] S. Dähne, D. Leupold, *Angew. Chem. Int. Ed.* **5.(12)**, 984 (1966).

[3] a) A. T. Ruiz, M. H. E. Bousquet, S. Pascal, G. Canard, V. Mazan, M. Elhabiri, D. Jacquemin, O. Siri, *Org. Lett.* **22.(20)**, 7997 (2020); b) S. Pascal, L. Lavaud, C. Azarias, G. Canard, M. Giorgi, D. Jacquemin, O. Siri, *Mater. Chem. Front.* **2.(9)**, 1618 (2018).

OC 02

Pathways to improve the chiroptical properties of helicene molecules via exciton coupling chirality.

Kais Dhbaibi[1*], Ludovic Favereau[1], Jeanne Crassous[1].
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Keywords: (Chirality, Helicene, Dyes, Exciton coupling, Circularly Polarized Luminescence)

Chirality describes an object that can exist as a pair of non-superimposable mirror-images. Despite its wellrecognized role in biological functions, chirality remains underexplored in the materials science area. One of the most intriguing properties of chiral molecules is their ability to interact specifically with left- and righthanded circularly polarized light either in absorption (Electronic Circular Dichroism, ECD) or in emission (Circularly Polarized Luminescence, CPL). The latter is becoming a focal point in several photonic applications, ranging from optical communication of spin information to novel display and imaging technologies.[1] Helicenes are polycyclic aromatic compounds with non-planar screw-shaped skeletons formed by ortho-fused benzene or other aromatic rings,[2] and can be regarded as valuable inherently chiral building blocks exhibiting good CPL activity.[3] In this communication, we will present how we took advantage of the exciton coupling chirality phenomenon to boost the CP emission of helicene molecules leading to strong and tunable CPL responses with high dissymmetry factors and the use of such chiral luminophore as active materials for the emission of dissymmetric CP light from organic light-emitting diodes (CP-OLEDs).[4] The direct generation of CPelectroluminescence would not only simplify the architecture of the OLEDs devices via the suppression of the optical polarization filter, but also, it can improve the contrast performances and the efficiency of conventional
2-D displays.[5]

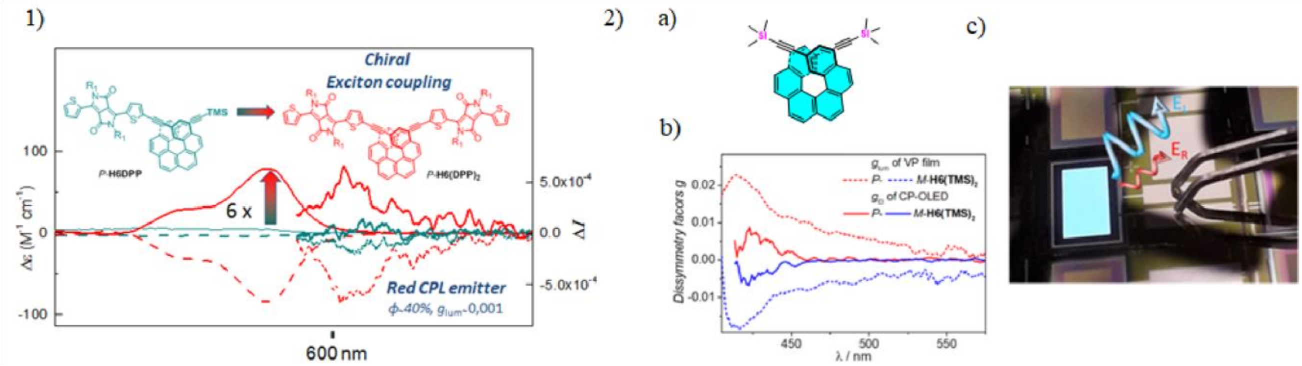

Figure 1. 1) Exciton coupling effect in the ECD and CPL spectra of diketopyrrolopyrrole-helicene derivatives. 2) Chemical structures of helicene luminophores used for CP-OLEDs b) Corresponding plots of the luminescence (from vapor deposition film) and electroluminescence dissymmetry factor, g_{lum} and g_{El}, respectively c) A picture of an operating CP-OLED.

[1] a) Brandt, J., Salerno, F., Fuchter., *Nat. Rev. Chem*. **2017**, *1*, 0045. b) Yang, Y., da Costa, R., Fuchter, M., Campbell, A.J., *Nature. Photon*. **2013**, *7*, 634. c) Shang, X., Wan, L., Wang, L., Gao, F., Li, H., *J. Mater. Chem. C*, **2022**, *10*, 2400.

[2] a) Y. Shen., C.F. Chen., *Chem. Rev.* **2012**, *112*, 1463. b) Dhbaibi, K., Favereau, L., Crassous., J., *Chem. Rev*. **2019**, *119*, 8846. c) J. Crassous, I.G.Stará, I. Starý, Helicenes -Synthesis, Properties and Applications, Wiley, **2022**.

[3] a) Sánchez-Carnerero, E.M., Agarrabeitia, A.R., Moreno, F., Maroto, B.L., Muller, G., Ortiz, M.J. and de la Moya, S., *Chem. Eur. J.*, **2015**, *21*, 13488 b) J. Crassous, in Circularly Polarized Luminescence of Isolated Small Organic Molecules, ed. T. Mori, Springer, Singapore, **2020**, 53.

[4] a) Dhbaibi, K.; Favereau, L., Srebro-Hooper, M., Jean, M., Vanthuyne, N., Zinna, F., Jamoussi, B., Di Bari, L., Autschbach, J., Crassous, J., *Chem. Sci*. **2018**, *9*, 735. b) Dhbaibi, K., Favereau, L., Srebro-Hooper, M., Quinton, C., Vanthuyne, N., Lorenzo, A., Roisnel. T., Jamoussi, B., Poriel, C., Cabanetos, C.; Di Bari, L.; Autschbach, J.; Crassous, J. *Chem. Sci*., **2020**,*11*, 567. c) Dhbaibi, K.; Abella, L.; Meunier-Della-Gatta, S.; Vanthuyne, N.; Roisnel, T., Jamoussi, B., Pieters, G., Racine, B., Quesnel, E., Autschbach, J., Crassous, J., Favereau, L., *Chem. Sci*., **2021**,*12*, 5522. d) Dhbaibi, K.; Shen, C., Jean, M., Vanthuyne, N., Roisnel, T., Górecki, M., Jamoussi, B., Favereau, L., Crassous, J., *Front. Chem*. **2020,** *8*, 237.

[5] a) Zinna, F., Giovanella, U. and Bari, L.D., *Adv. Mater*., **2015**, *27*,1791. b) Zinna, F., Pasini, M., Galeotti, F., Botta, C., Di Bari, L., Giovanella, U., *Adv. Funct. Mater*. **2017**, *27*, 1603719. b) D.-W. Zhang., M. Li., C.-F. Chen., *Chem. Soc. Rev*., **2020**, *49*, 1331 c) Frédéric, L., Desmarchelier, A., Favereau, L., Pieters, G., *Adv. Funct. Mater*. **2021**, *31*, 2010281.

OC 03

Hydrogen Atom Transfer: a powerful strategy for accessing α-amino ketyl radicals

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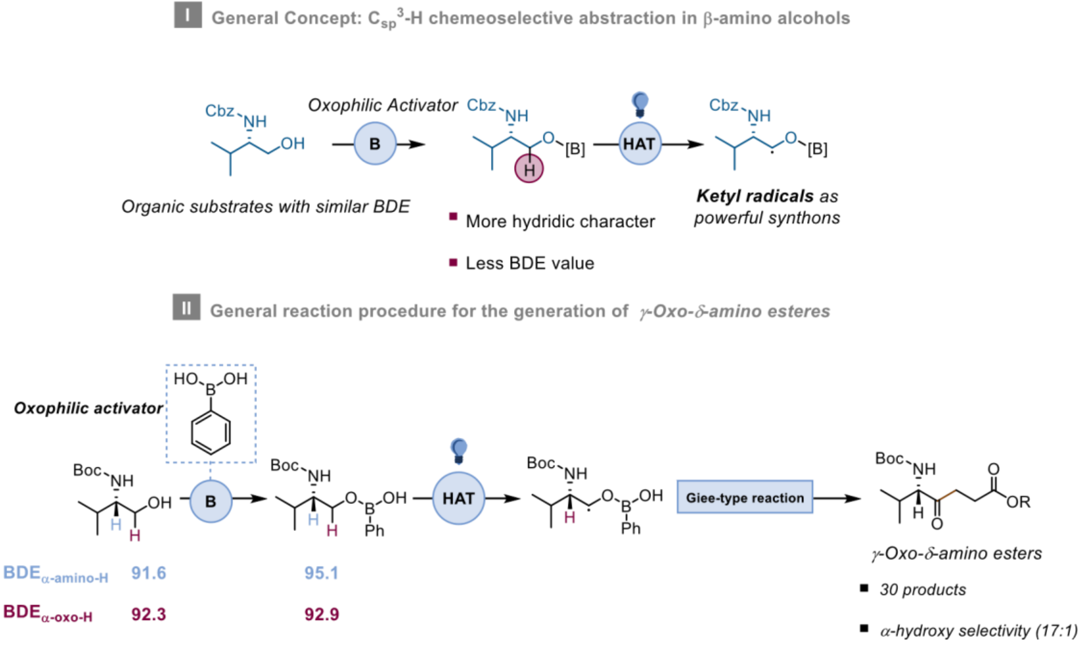
Keywords: Ketyl radicals, Photoredox catalysis, Hydrogen Atom Transfer (HAT), Density Functional Theory (DFT)

In recent years, hydrogen atom transfer (HAT) catalysis has emerged as one of the most forceful strategies to achieve high levels of selectivity in C–H functionalization reactions[1]. Mac Millan and co-workers reported pioneering processes in C-H bond functionalization, where they derivative C-H bonds adjacent to alcohol groups[2]. Subsequently, Kentaro Sakai's group further developed the same concept, although expanding the derivatizable substrates (amino acids and peptides) with the aid of an electron-deficient boron complex capable of better weakening the α-*oxo*-C-H bond in monohydric alcohols[3]. However, both strategies do not address a challenge that many organic compounds possessing C-H bonds of similar polarity and strength presents: the chemeoselective functionalization of a targeted hydrogen atom from a C_{sp}^{3}-H bond.

For this purpose, a visible-light photoredox catalytic strategy for the chemoselective abstraction of α-hydroxy C_{sp}^{3}–H bonds in β-amino alcohols was reported recently[4]. This catalytic approach takes advantage of the use of an oxophilic activator capable of lowering the bond dissociation energy (BDE) of α-*oxo*-C-H, and, in this way, contribute to the chemeoselective abstraction of α-*oxo*-C-H bond (Figure 1, I) in order to provide α-amino ketyl radicals, a versatile synthons. Thus, accessing to α-amino ketyl radicals enables the straightforward synthesis of □-oxo-□-amino esters. We also studied via Density Functional. Theory (DFT) calculations the key impact of the oxophilic activator in lowering BDE of α-*oxo*-C-H bond (Figure 1, II). The computed BDE of both α-*oxo*-C-H and α-*amino*-C-H show variations once the oxophilic activator is attached to β-amino alcohols, playing a central role in offering the high rates of α-hydroxy selectivity (17:1) provided experimentally.



I General Concept: C_{sp}^{3}-H chemoselective abstraction in β-amino alcohols

II General reaction procedure for the generation of γ-Oxo-δ-amino esteres

Figure 1: I: Simplified mechanism for the generation of ketyl radicals via HAT. II: Specific reaction conditions for accessing □-oxo-□-amino esters. BDE in kcal/mol.

[1] L. Capaldo, D. Ravelli, *European J Org Chem* **2017**, *2017*, 2056-2071.
[2] J. L. Jeffrey, J. A. Terrett, D. W. C. MacMillan, *Science* **2015**, *349*, 1532-1536.
[3] K. Sakai, K. Oisaki, M. Kanai, *Advanced Synthesis & Catalysis* **2020**, *362*, 337-343.
[4] K. Merkens, N. Sanosa, I. Funes-Ardoiz, A. Gómez-Suárez, *ACS Catalysis* **2022**, 13186-13192.

OC 04

Competitive Photoisomerization and Energy Transfer Processes in Fluorescent Multichromophoric Systems

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Keywords: multichromophoric system, multichromophores, FRET, molecular dynamics, DCM

A series of dicyanomethylene-4*H*-pyran (DCM)-based multichromophoric (multi-DCMs) were synthesized and their photophysical characteristics were measured. Based on the already known DCM *E*□*Z* photoisomerization and photoswitchable fluorescence properties, [1-3] the multi-DCM molecules exhibit multiple possibilities of intramolecular Förster resonance energy transfer (FRET) processes.

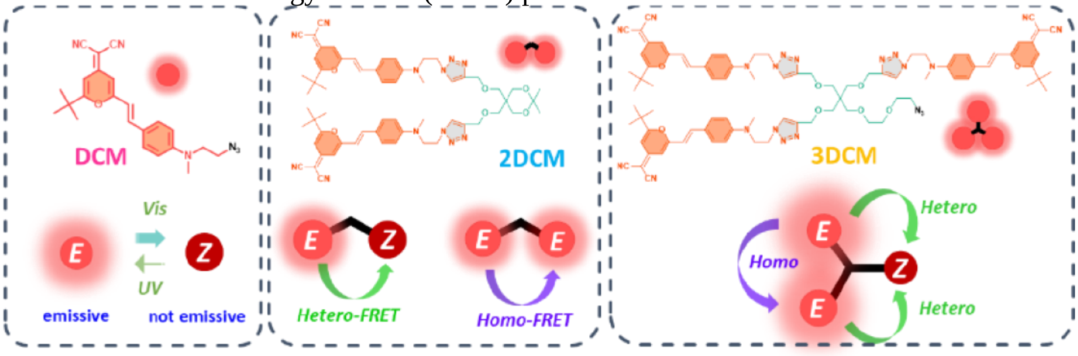

Figure 1. Structure of multi-DCMs and their corresponding isomerization, proposed FRET models.

The homo-FRET property was validated by the steady-state fluorescence anisotropy. The proposed homoFRET and hetero-FRET models were set up and run in the molecular dynamics (MD) simulations. The simulation results were analyzed by the trajectory-based techniques, and derived Markov state models, revealing the high FRET efficiencies and the conformational transition patterns between the DCM units.

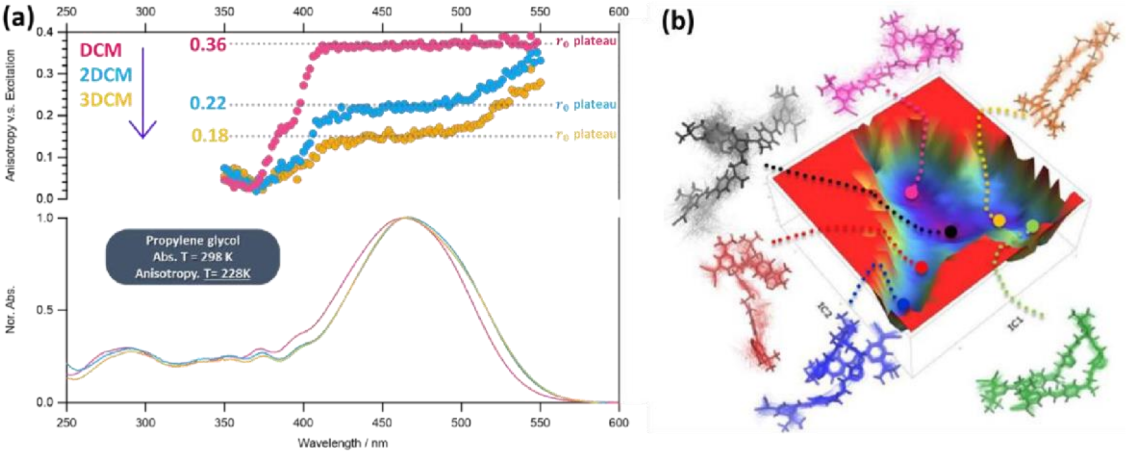

Figure 2. **(a)** Fluorescence anisotropy of DCM (pink), 2DCM (blue) and 3DCM (orange) in propylene glycol at -45°C, collected as a function of excitation wavelength. (Bottom) Absorption lines of DCM (pink), 2DCM (blue) and 3DCM (orange) in propylene glycol at -45°C. **(b)** 200 ns MD trajectories of *(EE)*-2DCM visualized on time-lagged independent component analysis free energy landscape and the corresponding clustered conformations.

[1] M. Lesiecki, F. Asmar, J. M. Drake, D. M. Camaioni. *J. Lumin.* **1984**, *31*, 546-548.

[2] L. Casimiro, S. Maisonneuve, P. Retailleau, S. Silvi, J. Xie, R. Métivier. *Chem. Eur. J.* **2020**, *26*, 14341-14350.

[3] Y. Zhou, S. Maisonneuve, L. Casimiro, P. Retailleau, J. Xie, F. Maurel, R. Métivier. *Phys. Chem. Chem. Phys.* **2022**, *24*, 6282-6289. [4] Y. Zhou, S. Maisonneuve, F. Maurel, J. Xie, Rémi Métivier. *Chem. Eur. J.* **2022**, e202202071.

OC 05

Light-responsive quinoline-foldamers with photo-switchable On/Off conductivity

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Keywords: Foldamer, conductivity, photoswitch, monolayer

Molecular electronics based on single molecules or small molecular ensembles aim to define molecular properties for implementation in molecular-based devices, such as diodes, transistors, and switches, among others. However, integrating molecules into electronic devices whose conductivity can be reproducibly and reversibly switched using light is a challenge that still needs to be addressed.[1] In this context, helical foldamers are attractive as they combine through space and through bond charge transport.[2] They can be interfaced with molecular recognition sites to yield devices whose conductivity is modulated by the binding of guest,[3] or interfaced with inorganic ions to modulate the nature of the charge transport.[4]

With this in mind, we aim to study the on/off conductance of systems based on helical quinoline foldamers with different lengths organized as single monolayers on gold surfaces. The reversible photocycloaddition of two anthracene moieties is used to covalently modulate the helical backbone of the foldamer chain, Figure 1. The photoresponse was studied in solution for a better understanding of the characteristics of the materials and by conductive AFM on single molecule layers.

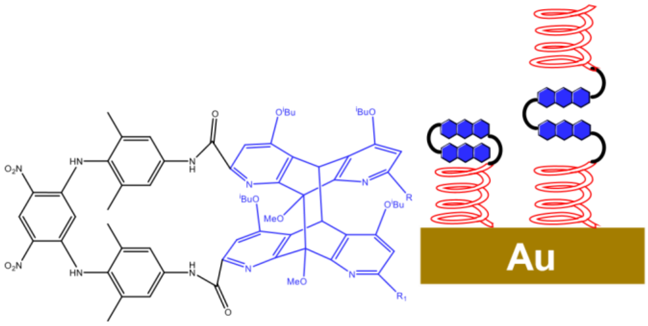

Figure 1-Photodimer of the anthracene moiety (R and R_1 remaining organic part of the foldamer) and foldamer monolayer representation on the gold surface.

[1] D. Roldan, V. Kaliginedi, S. Cobo, V. Kolivoska, C. Bucher, W. Hong, G. Royal, T. Wandlowski, J. Am. Chem. Soc., **2013**, 135, 5974−5977.

[2] Alejandro Méndez-Ardoy, Nagula Markandeya, Xuesong Li, Yu-Tang Tsai, Gilles Pecastaings, Thierry Buffeteau, Victor Maurizot, Luca Muccioli, Frédéric Castet, Ivan Huc, Dario M. Bassani, Chem. Sci. **2017**, 8, 7251 – 7257.

[3] Pedro Mateus, Antoine Jacquet, Alejandro Méndez-Ardoy, Alice Boulloy, Brice Kauffmann, Gilles Pecastaings, Thierry Buffeteau, Yann Ferrand, Dario M. Bassani, Ivan Huc, Chem. Sci., **2021**, 12, 3743 – 3750.

[4] Jinhua Wang, Barbara Wicher, Alejandro Méndez-Ardoy, Xuesong Li, Gilles Pecastaings, Thierry Buffeteau, Dario M. Bassani, Victor Maurizot, Ivan Huc, Angew. Chem. Int. Ed., **2021**, 60, 18461 – 18466.

OC 06

Synthesis and Characterization of Photo-activatable Systems

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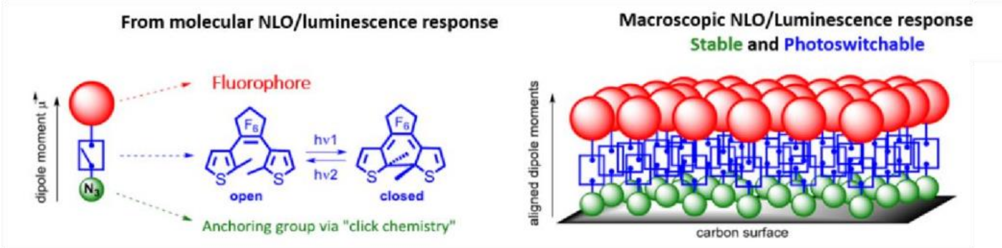
Keywords: *Photoswitchable materials, photophysics,nonlinear optics, luminescence, grafting on surface*

Light responsive molecular materials constitute an extremely active research field driven by the significant progresses conducted in a wide panel of applications such as light displays (OLEDs), optoelectronics (OFETs), bio-imaging [1] and light conversion (solar cells, photo-catalysis).[2] In the particular case of data storage, the strategy proposed is based on the preparation of a molecular material that display stable and light-activatable nonlinear optical (NLO) responses and/or luminescence properties. The material will be formed by a monolayer of chromophores grafted on a surface, through alkyne-azide click chemistry. The combination with a photochromic unit will allow a reversible light triggered reaction to write, store and read information with light as unique external stimulus due to its easy and contactless application. Diarylethenes (DAEs) are among the most commonly used classes of photochromic compounds *(Figure 1)*. Especially, dithienylethene (DTE) are known for their excellent thermal stability and fatigue resistance. [3] The general design of the targeted chromophores is divided into three parts: an anchoring function, a linker and the photo-active unit. These chromophores can be organic [4] or organometallics.

a)



b)

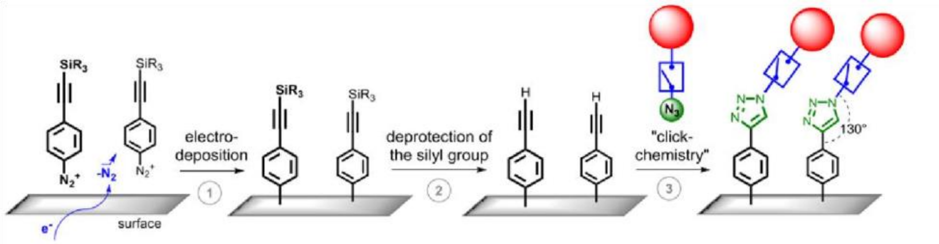


Figure 1. General molecular design(a) and the grafting methodology(b).

In this presentation, I will illustrate the synthetic approach of formation of photo-switchable molecular material symbolized by the diarylethene moiety terminated with azide terminal group and their grafting results will be clearly discussed. Moreover, a fluorophore will be inserted to DTE framework inorder to regulate the luminescence properties upon photochromism.

[1] Yeung, M. C.-L.; Yam, V. W.-W., *Chem. Sci.* **2013,** *4,* 2928-2935.
[2] Wegner, H. A., *Angew. Chem. Int. Ed.* **2012,** *51*, 2281-2281.
[3] a) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake *Chem. Rev.* **2014**, *114*, 12174−12277. b) H. Zhao, E. Garoni, T. Roisnel, A. Colombo,

C. Dragonetti, D. Marinotto, S. Righetto, D. Roberto, D. Jacquemin, J. Boixel, V. Guerchais *Chem. Commun*., **2016**, *52*, 9833 – 9836.c) H.Zhao,E.Garoni, T.Roisnel, A.Colombo, C.Dragonetti ,D.Marinotto, S.Righetto, D.Roberto, D.Jacquemin, J.Boixel, V. Guerchais *Inorg. Chem.* **2018**, *57*, 7051−7063
[4] a) H.Guo, M. L. Muro-Small, S.Ji, J. Zhao, F. N. Castellano, *Inorg. Chem.* **2010**, *49*, 6802–6804. b) F. Zhong, J. Zhao, *Eur. J. Inorg. Chem.* **2017**, *44*, 5196–5204.

OC 07

TUNABLE PHOSPHORESCENCE *VIA* THE STRUCTURE DESIGN OF CYCLOMETALATED Pt(II) COMPLEXES

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Keywords: Organic light-emitting diodes (OLEDs); Phosphorescence; Cyclometalated Pt(II) complexes; Diazines

Organic light-emitting diodes (OLEDs) have gained a lot of attention as effective candidates for flat panel display technologies and solid-state lighting due to a number of following advantages such as: small size, flexibility, brightness, fast response time and superior viewing angle.[1,2] Phosphorescent heavy-metal complexes, such as iridium(III) and platinum(II) complexes with strong spin-orbit coupling are able to efficiently harvest both singlet and triplet electro-generated excitons, thus opening the possibility to achieve theoretically 100% internal quantum efficiency in such devices.[3] Cyclometalated platinum(II) complexes have attracted a lot of interest because of their interesting coordination geometry and rich photochemical and physical properties, which make them useful as efficient phosphorescent materials for fabrication of OLEDs.[4] Pt(II) metal center are four-coordinated that can accommodate bidentate, tridentate, or tetradentate chelating ligands, with ancillary ligands where necessary, that allows considerable flexibility in engineering a desired complex for application as light emitting materials in OLEDs.[5] It is easy to alter electronic structures and photophysical properties of platinum complexes by modification of the coordinated ligands.[6] In this communication, we will describe the synthesis of the new series of phosphorescent cyclometalated platinum(II) complexes, containing **C^N^N**[7] and **N^C^N**[8] **tridentate** and **C^N**[9] **bidentate coordinating ligands, based on diazines**. An **appropriate functionalization of the cyclometalated ligand and the choice of the ancillary ligand, allow to tune the photophysical and electrochemical properties of these complexes**. The influence of various structural modification on photophysical properties had been thoroughly studied and structure properties relationships were highlighted.

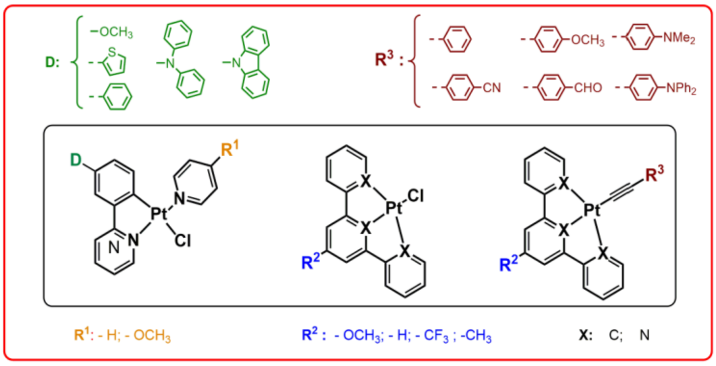

Figure 1. Chemical structures of the investigated tridentate C^N^N, N^C^N and bidentate C^N cyclometalated Pt(II) complexes.

[1] S.R. Forrest, Nature, **2004**, 428, 914-918.
[2] B. P. Pamchandra, Renewable and Sustainable Energy Reviews, **2020**, 133, 110043-110069.
[3] C. Cebrian, M. Mauro, Beilstein J. Org. Chem., **2018**, 14, 1459-1481.
[4] E. Baggaley, J. A. Weinstein, J.A.G. Williams, Coord. Chem. Rev., **2012**, 57, 1762-1785.
[5] H. Shouquan, C.Jeffrey, A. K. V. Dileep, Asian J. Org. Chem., **2015**, 4, 1210-1245.
[6] L. Baoning, L. ZHenjie, Y. Huijie, L. Yongguang Mol. Syst. Des. Eng,, **2020**, 5, 1578-1605.
[7] M. Hruzd, S. Gauthier, J. Boixel, S. Kahkak, N. Le Poul, J-Y Saillard, S. Achelle, F. Robin-Le Guen Dyes Pigm., **2021**, 194, 109622-109633.
[8] M. Hruzd, N. le Poul, M. Cordier S. Kahlal, J-Y Saillard, S. Achelle, S. Gauthier, F.Robin-le Guen, Dalton Trans., **2022**, 51, 5546-5560.
[9] M. Fecková, S. Kahlal, T. Roisnel, J-Y Saillard, J. Boixel, M. Hruzd, P. Le Poul, S. Gauthier, F. Robin-le, F. Bureš, S. Achelle, Eur. J. Inorg. Chem., **2021**, 16, 1592 - 1600.

OC 08

SYNTHESIS OF AZOBENZENE-BASED SACCHARIDES AND INVESTIGATION OF THEIR PHOTOSWITCHING PROPERTIES IN WATER

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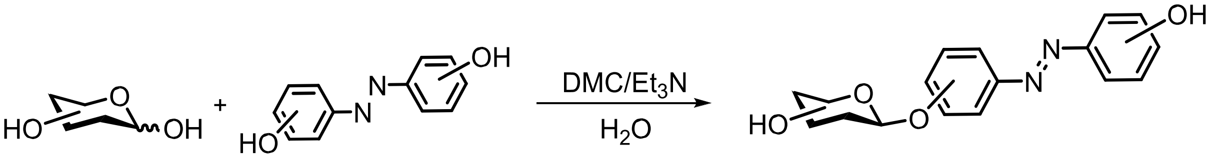
Keywords: photoswitches, glycosyl azobenzenes, unprotected sugars, photoswitching behaviors, water-soluble

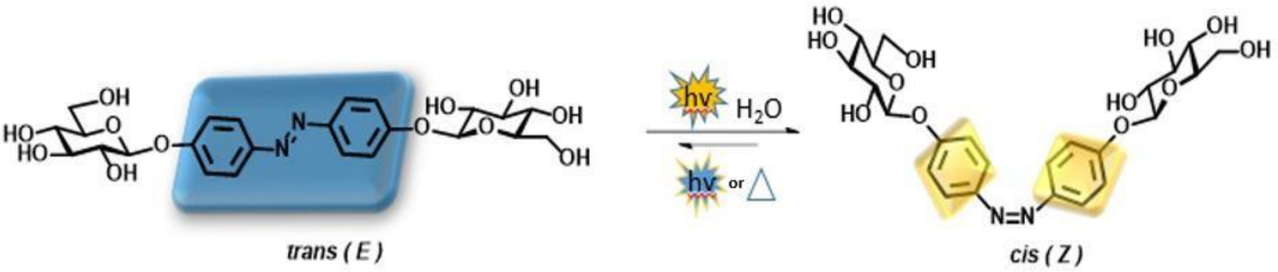
Molecular photoswitches with photoswitching ability in aqueous medium are highly demanded for biological applications and photopharmacology.[1, 2] However, the commonly developed photoswitches like azobenzenes, diarylethenes are barely soluble in water. Linking carbohydrates to a photoswitching unit is an interesting approach to obtain water-soluble photochromic compounds.

Since several years, azobenzene-functionalized photoswitchable glycoconjugates have been developed for light-controlled carbohydrate-protein interactions,[3] cell adhesion,[4] enzyme inhibitors[5] and glycolipid mimics,[6] and so on. However, glycosylation with unprotected sugars in aqueous media remains a challenging task.[7] Recently, DMC (2-chloro-1,3-dimethylimidazolinium chloride) mediated glycosylation of unprotected sugars with phenols in aqueous medium has shown promising results.[8]

As a continuing interest in the development of photoswitchable carbohydrates,[9] we are developing the DMC-mediated glycosylation of hydroxyazobenzene with unprotected sugars (Scheme **1**). After optimization of reaction conditions, we are able to prepare a series of water-soluble glycosyl azobenzenes. Furthermore, the synthesized glycosyl azobenzenes displayed remarkable photoswitching behavior in water (Scheme **2**). These new results will be presented.



Scheme 1: DMC-mediated glycosylation of hydroxy-azobenzene derivatives.



Scheme 2: Isomerization of glycosyl azobenzene upon light and heat.

[1] Volarić, J.; Szymanski, W.; Simeth, N. A.; Feringa, B. L. *Chem. Soc. Rev*. **2021**, *50*, 12377. [2] Fuchter, M. J. *J. Med. Chem*. **2020**, *63*, 11436.

[3] Kanamori, T.; Yuasa, H.; et al, *Bioorg. Med. Chem. Lett*. **2020**, *30*, 126960.

[4] Despras, G.; Lindhorst, T. K.; *et al, Chem. Bio. Chem.* **2019**, *20*, 2373.

[5] (a) Díaz-Lobo, M.; Ferrer, J. C.; *et al, Org. Biomol. Chem*. **2015**, *13*, 7282; (b) Rustler, K.; König, B.; *et al, Org. Biomol. Chem.* **2018**, *16*, 7430.

[6] Hartrampf, N.; Seki, T.; Baumann, A.; *et al*, *Chem. Eur. J.* **2020**, *26*, 4476.

[7] Downey, A. M.; Hocek, M. *J. Org. Chem.* **2017**, *13*, 1239.

[8] Qiu, X.; Fairbanks, A. *J. Org. Biomol. Chem*. **2020**, *18*, 7355.

[9] (a) Lin, C.; Maisonneuve, S.; Métivier, R.; Xie, J. *Chem. Eur. J.* **2017**, *23*, 14996; (b) Lin, C.; Maisonneuve, S.; Theulier, C.; Xie, J. *Eur. J. Org. Chem.* **2019**, 1770; (c) Kim, Y.; Xie, J. *et al*, *ACS Appl. Mater. Interfaces* **2020**, *12*, 52146; (d) Lin, C.; Jiao, J.; Mallétroit, J.; Maisonneuve, S.; Xie, J. *Chem. Commun.* **2020**, *56*, 3261; (e) Jiao, J.; Maisonneuve, S.; Xie, J. *J. Org. Chem.* **2022**, *87*, 8534.

OC 09

Design, characterization and evaluation of a lab-made photoreactor: a first step towards standardized procedures in photocatalysis.

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Keywords: photochemistry • actinometry • lab-made reactor • reproducibility • 3D-printing

For the last ten years, photochemistry has known a renewal with the emergence of new photoredox approaches along with new powerful artificial sources of light. Significant pioneering works by MacMillan, Yoon and others paved the way for the description of numerous chemical transformations[1]. However, the drawback of the fast growth of this field is the lack of homogeneous reporting: the wavelength used, the light power received are, for example, not always described in the procedures, nor determined. This lacunar information hampers the development of standardized procedures which would guarantee the reproducibility of the reactions.

With the objective of furnishing a standardized and easy-to-use setup, a reactor was designed and 3D-printed in our lab. The light power received at different positions was measured by means of a chemical actinometer[2]. Power homogeneity over a same iso-line was assessed along with the possibility to run up to 6 reactions simultaneously with one lamp. Variation of the environment, *ie.* reflective coating, water bath, revealed the dramatic influence of seemingly insignificant parameters over the actual power received and thus upon the upcoming of the reactions.

This new reactor, fully characterized in terms of optical intensity, offers an easy and affordable approach to photochemistry[3]. The homogeneity of the light power induces increased reproducibility, and the possibility to tune the intensity received depending on the environment make the study of the power/yield relation easier.

Figure 1. 3D view of the conceived reactor (left). Reactor in use (right).

[1] Selected reviews : a) M. Oelgemöller *Chem. Rev.* **2016**, *116*, 9664-9682. b) N. A. Romero, D. A. Nicewicz *Chem. Rev.* **2016**, *116*, 10075-10166. c) K. L. Skubi, T. R. Blum, T. P. Yoon *Chem Rev.* **2016**, *116*, 10035-10074. d) L. Candish, K. D. Collins, G. C. Cook; J. J. Douglas, A. Gómez-Suarez, A. Jolit, S. Keess *Chem Rev.* **2022**, *122*, 2907-2980. e) A. Y. Chan, I. B. Perry, N. B. Bissonette, B. F. Buksh, G. A. Edwards, L. I. Fryes, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley; N. L. Reed, H. A. Sakai, C. P. Seath, D. W. C. MacMillan *Chem. Rev.* **2022**, 122, 1485-1542.

[2] a) C. A. Parker *Proc. R. Soc. Lond. A* **1953**, *220*, 104-116. b) C. G. Hatchard, C. A. Parker, *Proc. R. Soc. Lond. A* **1956**, *235*, 518-536. c) H. J. Kuhn, S. E. Braslavsky, R. Schmidt *Pure Appl. Chem.* **2004**, *76*, 2105–2146. d) M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi Chemical Actinometry *in Handbook of Photochemistry,* 3rd edition, CRC Press : Boca Raton, **2006**. e) J. Rabani, H. Mamane, D. Pousty, J.R. Bolton *Photochem. Photobiol* **2021**, *97*, 873-902.

[3] Publication in preparation. *.step (conception) and *.stl (printing) files available open source on request.

OC 10

Symmetry drives fused nanographene-metalloporphyrin conjugates photophysics

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Keywords: symmetry, stimulated emission, catalysis, panchromatic, nanographene, solar cells, metalorganic molecules.

Femtosecond optical transient absorption spectroscopy is employed to study, for the first time, photoexcited carrier relaxation in □-,meso-,□-triplyfused porphyrin-nanographene conjugates **AS** and **S** [1]. These compounds are panchromatic nanographenes (NGs) with an onset of absorption matching the solar spectrum, making these compouns suitable candidate for high efficiency solar cells.

Symmetry has a profound effect of the excited state pathways in these molecules. The symmetric structure, (**S** orange region Fig.1a), depicts a strong picosecond excited state funnelling towards the Ni-Porphyrin centre, which preserves an electronic metal centred character, in contrast with the larger interplay of the nanographene on the absorption spectrum. The asymmetric structure instead (**AS** orange region Fig.1a), displays excited-state among the fused conjugated ribbon, allowing the appearance of stimulated emission and photoluminescence at 955 nm (1.3 eV) as well as an overall faster decay kinetics than in **S**. Hence, the substitution symmetry can be used as a versatile tool for tuning the opto-electronic properties of these NGs.

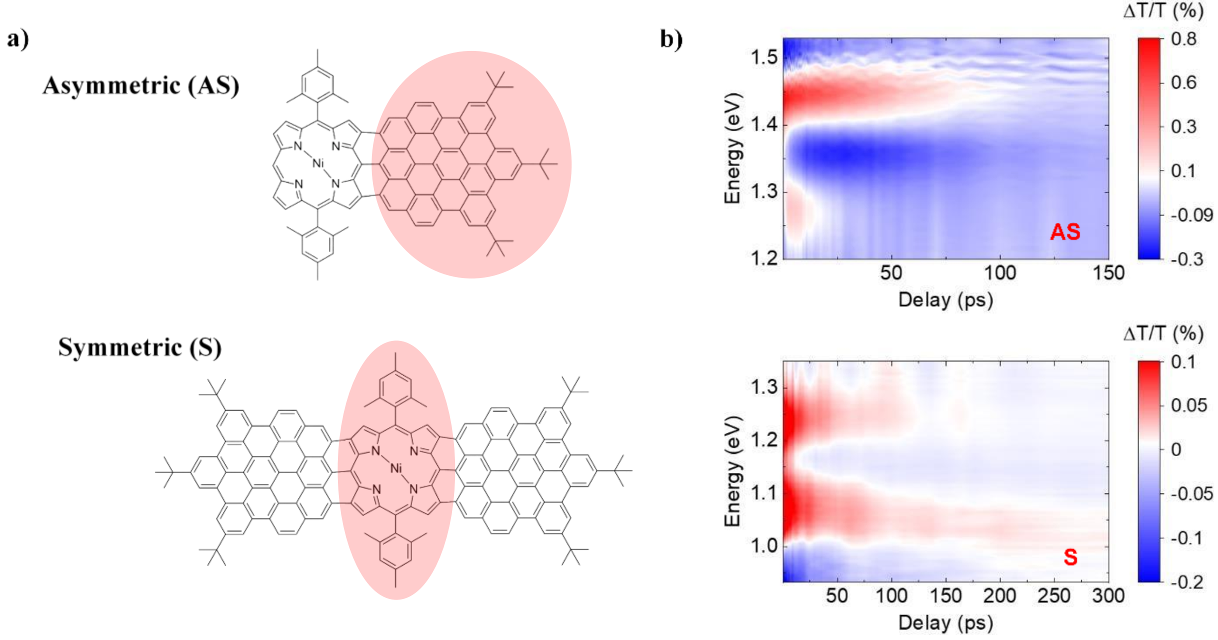

Figure 1. **a)** Structures of triply fused porphyrin-nanographene conjugates **AS** and **S** [1], the orangre regions indicate the deexcitation regions in each molecule. **b)** Differential transmission signal obtained for conjugates **AS** and **S** after pumping with a 778 nm laser and 605 nm respectively.

[1] Q. Chen, L. Brambilla, L. Daukiya, K. S. Mali, S. De Feyter, M. Tommasini, K. Müllen, A. Narita, Angew. Chem., **2018**, 57, 1123.

OC 11

MECHANICAL EFFECT PRODUCED BY PHOTOSWITCHABLE REACTIONS : INSIGHTS FROM MOLECULAR SIMULATIONS

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Keywords: Photonastic materials, Photochrome, Phomechanical process

Photonastic materials are able to transfer light to mechanical energy through macroscopic transformations. Recently, the macroscopic bending of a polymeric material based on a 4,4'-dihydroxyazobenzene photoswitch embedded in a chitosan matrix was observed under 355 nm irradiation [1]. This photonastic system was also able to convert efficiently light to mechanical work.

In this framework, to understand and optimize the solar ❼ mechanical energy conversion, computational chemistry can provide useful insights on the atomistic/molecular scale processes involved in the photonastic process. We propose here to consider a model system based on a 4,4'-dihydroxyazobenzene photoswitch embedded in a model polybutadiene matrix. Relying on molecular dynamics (MD) simulations and time-dependent density functional theory (DFT) calculations [2], we will present a detailed analysis of (i) the impact of the polymer matrix on the properties of the *cis* and *trans* isomers (Figure 1) and (ii) the impact of the photochromic reaction on the polymer environment.

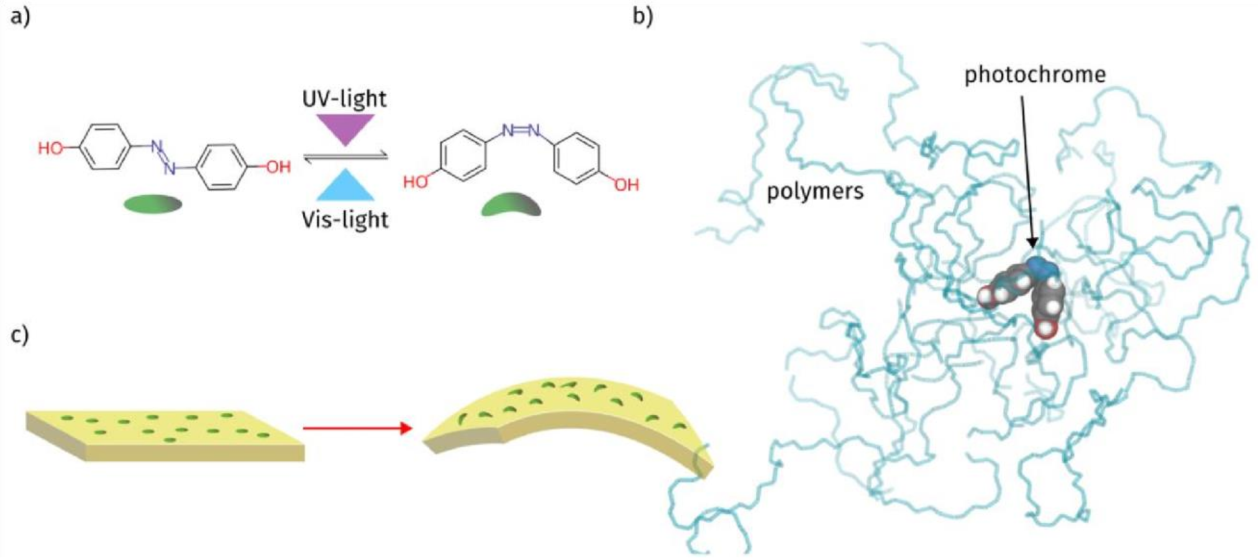

Figure 1. (a) Photoswichable reaction between cis and trans4,4'-dihydroxyazobenzene. (b) Photochrome in the polymeric matrix. (c) Schematic representation of the photonastic effect. [1] Yu, C. Y. *et al.*/ *Chinese J. Polym. Sci.* **2020**, 39. 417-424.

[2] Le Bras, L. *et al.*/ J. Chem. Therry Comput. **2020**, 7017-7032

OC 12

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

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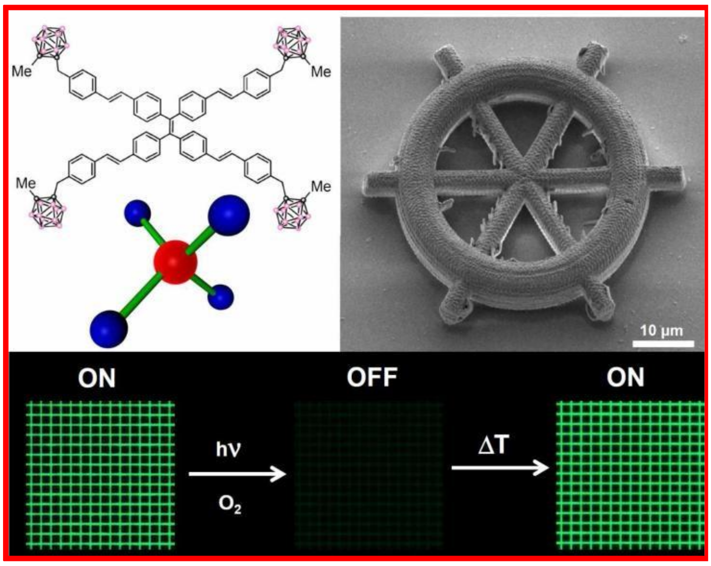
Keywords: Two-Photon Absorption, 3D-Stereolithography, Stimuli Responsive Photomaterials

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 twophoton 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 crosslinking. 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.



[1] C.N. LaFratta, J.T. Fourkas, T. Baldacchini, R.A. Farrer, Angew. Chem. Int. ed 46 (2007) 6238-6258.

[2] J. Fischer, M. Wegener, Laser Photonics Rev. 7 (2012) 22-44.

[3] G. Kenanakis, A. Xomalis, A. Selimis, M. Vamvakaki, M. Farsari, M. Kafesaki, C.M. Soukoulis, E.N. Economou, ACS Photonics 2 (2015) 287-294.

[4] R. Mhanna, N. Durand, P. Savel, H. Akdas-Kiliç, S. Abdallah, D.-L. Versace, O. Soppera, J.-L. Fillaut, N. Sojic, J.-P. Malval, Chem Comm. 58 (2022) 9678-9681.

[5] K. Parkatzidis, M. Chatzinikolaidou, M. Kaliva, A. Bakopoulou, M. Farsari, M. Vamvakaki, ACS Biomater. Sci. Eng. 5 (2019) 6161-6170.

[6] J. Torgersen, X.-H. Qin, Z. Li, A. Ovsianikov, R. Liska, J. Stampfl, Adv. Funct. Mater. 23 (2013) 4542-4554.

OC 13

Investigation of the Superoxide Anion Sensing Potential of Brominated Coelenterazine Analogs

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Keywords: Coelenterazine, Chemiluminescence, Superoxide Anion, Reactive Oxygen Species, Sensing

Superoxide anion is a reactive oxygen species (ROS) of biological interest, as it plays a role in both intra- and intercellular signaling.[1] Superoxide anion is also associated with conditions such as inflammation and cancer. Given this, the research community has given attention to the development of new sensing methods for the selective and sensitive determination of this ROS species.[1]

Among these approaches, chemiluminescence (CL) has been showing great potential. CL is an interesting process in which light is emitted due to a chemical reaction, without the need for photoexcitation, which leads to high signal-to-noise.[2] Among different CL systems, that of marine Coelenterazine has been attracting attention as a superoxide anion probe, as its CL reaction can be triggered solely by this ROS species.[1] However, its light-emission intensity is typically reduced in aqueous media,[3] which can prevent its use as a ROS probe.

Our team has studied the Coelenterazine system and in recent years has discovered that the bromination of its scaffold can provide this system with new and enhanced properties, such as anticancer activity.[2] More relevantly, the introduction of bromine heteroatoms can also lead to enhanced CL emission in an aqueous solution, when triggered by a superoxide anion, which allows this system to be used as a dynamic and sensitive superoxide anion probe. [4-6]

Herein, in this study, we investigate the CL reaction of different brominated Coelenterazine analogs using luminometry and UV-Vis and fluorescence spectroscopy. Our aim is the determination of relevant structure-activity relationships regarding the superoxide anion-induced CL emission by these compounds, as well as to understand the reason behind their enhanced emission. These results should help to guide future developments of Coelenterazine-based compounds as CL probes for superoxide anion.

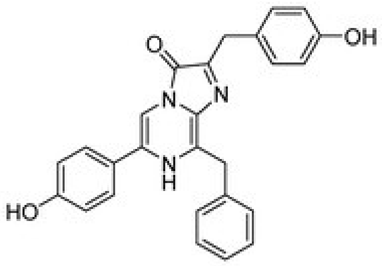

Figure 1. Molecular structure of native Coelenterazine.

Acknowledgements: "*Fundação para a Ciência e Tecnologia*" (FCT) for funding of projects PTDC/QUI-QFI/2870/2020, UIDB/00081/2020 (CIQUP), LA/P/0056/2020 (IMS), as well as CEECINST/00069/2021 (L.P.d.S.).

References:

[1] Bronsart, L.L. et al. Molecular imaging and biology, **2016**, 18, (2), 166-171
[2] Pinto da Silva, L. et al. European Journal of Medicinal Chemistry, **2019**, 183, 111683
[3] Lourenço, J.M. et al. Journal of Luminescence, **2018**, 194, 139-145
[4] Silva, J.P. et al. Chemosensors, **2022**, 10, (5), 174
[5] Silva, J.P et al. Journal of Photochemistry and Photobiology A: Chemistry, **2023**, 434, 114228
[6] Sousa, S. et al. International Journal of Molecular Sciences, **2022**, 23, 8490

OC 14

EVALUATION OF PH AND STOICHIOMETRY OF THE N-DOPANT EFFECT INTO CARBON DOTS PROPERTIES

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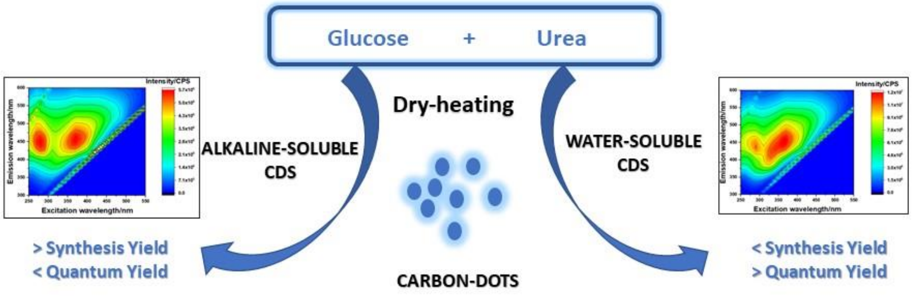
Keywords: Carbon dots, N-doping, nanoparticles, luminescence.

Carbon-based nanoparticles, Carbon dots (CDs), have attracted significant attention from the research community due to their remarkable luminescence properties.[1] Their synthesis by bottom-up strategies is quite flexible, as tuning the reaction precursors and synthesis procedures can lead to an endless number of CDs with distinct properties and/or applications. High fluorescence quantum yields (QY_{FL}) are generally a necessity for suitable performances by the employed CDs. One commonly employed strategy to improve the fluorescent properties of synthesized CDs is heteroatom-doping using precursors containing desired heteroatoms (as N-doping).[2]

In this work, we report the synthesis and systematic investigation of a variety of N-doped CDs, obtained from the dry heating of the same solid mixtures precursors, glucose (as carbon source) and urea (as N-dopant) with different molar ratios, with two main objectives: study the role of stoichiometry on the optical properties and composition of CDs and investigate the formation of possible alkaline-responsive nanoparticles and the potential of this procedure for obtaining CDs with higher synthesis yield. We have characterized the prepared N-doped CDs by UV-Vis, fluorescence and X-Ray photoelectron (XPS) spectroscopy, and high-resolution transmission electron microscopy (HR-TEM), as well as by assessing the thermal stability of the nanoparticles.

We have found that this fabrication process generates two types of CDs, one readily soluble in water and other only soluble at basic pH. The latter was characterized by higher synthesis yields, and lower QY_{FL} and thermal stability, when comparing with the former. Moreover, the stoichiometry of the N-dopant does not appear to be correlated with the QY_{FL} of the obtained CDs.



Acknowledgments: The Portuguese "*Fundação para a Ciência e Tecnologia*" (FCT, Lisbon) is acknowledged for funding of project PTDC/QUIQFI/2870/2020, R&D Units CIQUP (UIDB/00081/2020) and Associated Laboratory IMS (LA/P/0056/2020). Luís Pinto da Silva acknowledges funding from FCT under the Scientific Employment Stimulus (CEECINST/00069/2021). Diana Crista acknowledges FCT for funding her PhD grant SFRH/BD/144423/2019.

[1] D. M. A. Crista, J. C. G. Esteves da Silva and L. Pinto da Silva, *Nanomaterials*, **2020**, 10, 1219.

[2] D. M. A. Crista, J. C. G. Esteves da Silva and L. Pinto da Silva, *Nanomaterials*, **2020**, 10, 1316.

OC 15

Sulfur-doped carbon nitride hybrid materials tested under green light for photoelectrocatalytic benzylamine oxidation and oxygen evolution reactions

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Keywords: carbon nitride, purpald, sulfur, benzylamine photooxidation, oxygen evolution

High-performing materials will dictate the pace of reinventing industrial chemical processes to achieve carbon neutrality [1]. Visible-light photoelectrocatalysts from abundant resources will play a key role in exploiting solar irradiation [2]. Anionic doping via pre-organization of precursors and further co-polymerization creates tuneable, extrinsic semiconductors. Triazole derivative-purpald, an unexplored precursor with sulfur (S) container, combined in different initial ratios with melamine during one solid-state polycondensation with two thermal steps yields hybrid S-doped carbon nitrides (C_3N_4).

The series of S-doped/C_3N_4-based materials showed enhanced optical, electronic, structural, textural, and morphological properties and exhibited higher performance in organic benzylamine photooxidation, oxygen evolution, and similar energy storage (capacitor brief investigation) [3]. 50M-50P exhibited the highest photooxidation conversion yield (84±3%) of benzylamine to imine at 535 nm – green light for 48h (**Figure 1**), due to an extra discrete shoulder reaching ~700 nm, an unusual high sulfur content, preservation of crystal size, new intraband energy states, rare deep structural defects by layer distortion, hydrophobic surface, low porosity, and 1016 nm pores. An in-depth analysis of S doping was investigated coupling x-ray photoelectron spectroscopy, transmission electron microscope, and elemental analysis, providing insights on bonds, distribution, and surface/bulk content. This work contributes to the development of disordered photocatalysts with long-visible-light range for solar energy conversion and storage.

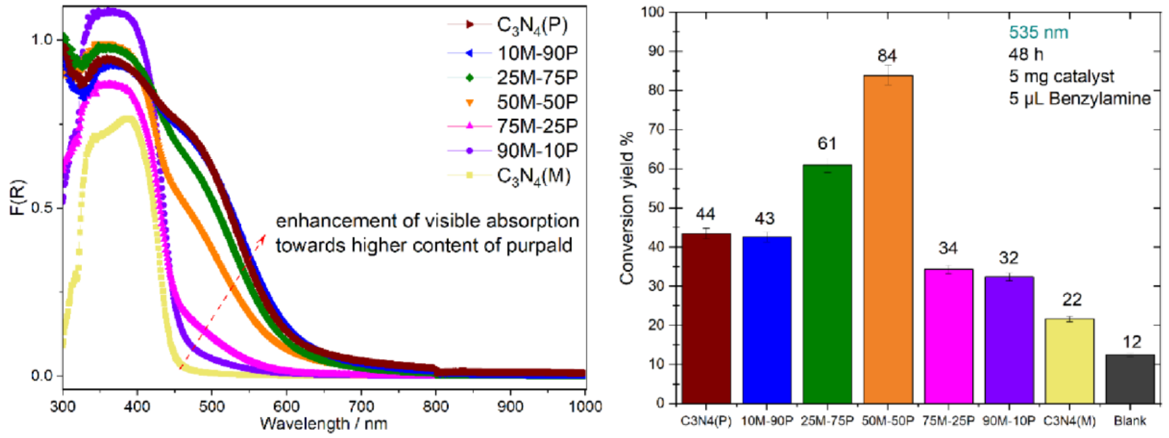

Figure 1. **Left)** Kubelka-Munk UV-vis spectra. **Right)** Photooxidation of benzylamine including the reaction conditions.

[1] Mark Isaacs, Julio Garcia-Navarro, Wee-Jun Ong, Pablo Jiménez-Calvo, Global Challenges, **2022**, production.

[2] Pablo Jiménez-Calvo, Valérie Caps, Valérie Keller, Renewable and Sustainable Energy Reviews**, 2021**, 149, 111095

[3] Maria Jerigova, Yevheniia Markushyna, Ivo F. Texeira, Bolortuya Badamdorj, Mark Isaacs, Daniel Cruz, Iver Lauerman, Miguel Ángel MuñozMárquez, Nadezda V. Tarakina, Nieves Lopez Salas, Aleksandr Savateev, Pablo Jimenéz-Calvo, ChemRxiv Cambridge Open Engage, **2022**

OC 16

PHOTOCHEMICAL IMAGING OF NEAR-FIELD AND DISSYMMETRY FACTOR IN CHIRAL NANOSTRUCTURES

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Keywords: azopolymer, photochemistry, chirality, nanostructures.

Chiral nanostructures interact differently with right and left circularly polarized light. Moreover, they exhibit enhanced electric and magnetic near-fields leading to the so-called superchirality. This effect can be used for the detection of chiral biological objects with high enantio-sensitivity. Indeed, the optical chirality C is correlated with the rate of excitation of the chiral molecule [1], so that increasing the optical chirality at the location of the molecule can significantly improve its detection [2]. We present here a subwavelength imaging approach that is based on the interaction between the highly exalted near-field of chiral nanoparticles and an azobenzene molecule (DR1, disperse red 1) grafted to a polymeric chain (i.e. PMMA). Under illumination, the azobenzene molecules (DR1) undergo photo-isomerization cycles, which induce a displacement of matter inducing measurable topographical modifications that can be tracked using atomic force microscopy. Therefore, we obtain in the polymer a map of the near-field of the chiral nanostructures [3]. We recently demonstrated that chiral effects and field dissymmetry in plasmonic nanostructures can be imaged with this technique [4]. Here, we apply photochemical imaging to chiral metallic nanostructures composed of two coupled gold nanorods. Each rod has a length of 140 nm, a width of 70 nm and a height of 50 nm. They are separated by a 30 nm wide gap and are shifted with respect to each other by a distance '***S***' along their long axis. We show that the near-field chiral response can be imprinted in the photopolymer. It is shown that it is possible to experimentally map the near-field dissymmetry factor, which is the contrast in the local near-field response of the object under RCP and LCP excitation.

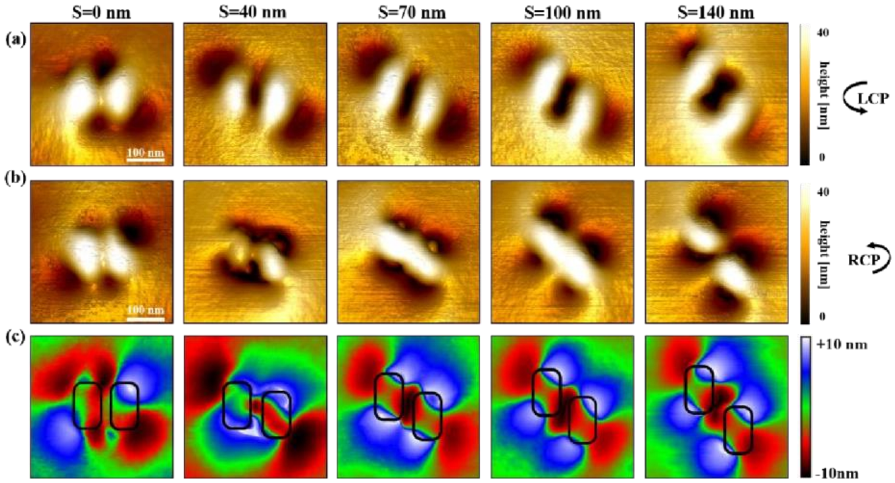

Figure 1. (a,b) AFM images after irradiation by the left (LCP) and right (RCP) polarization. (c) V-factor maps.

References

[1] Tang, Y. And Cohen, A. E. 2010. *Phys. Rev. Lett*. 104, 163901.

[2] Hendry, E. Carpy, T. Johnston, J. Popland, M. Mikhaylovsky, R. V. Lapthorn, A. J. Kelly, S. M. Barron, L. D. Gadegaard, N. and Kadodwala, M. 2010. *Nature Nanotech*. 5, 783.

[3] Plain, J. Wiederrecht, G. P. Gray, S. K. Royer, P. and Bachelot, R. 2013. *J. Phys. Chem. Lett*. 2013, 4, 2124-2132. [4] Horrer, A. Zhang, Y. Gérard, D. Beal, J. Kociak, M. Plain, J. and Bachelot, R. 2020. *Nano Lett*. 20, 509–516.

OC 17

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

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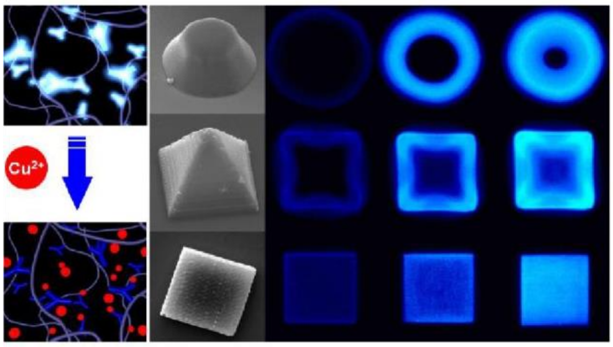
Two-photon stereolithography (TPS) is a layer-by-layer assembly technique that has proved to be a powerful tool for the fabrication of intricate 3D microstructures with very high spatial resolution[1]. Due to TPS numerous and versatile applications, the conception of two-photon active materials according to the established structureproperty relationships[2-4] has gained great interest recently.

In line with these structure-property relationships, we have elaborated a series of multi-branched triphenylamines photoinitiators[5-6] which incorporate an electron donor group (triphenylamine) decorated with electron acceptor group (ketone) and with substituents such as anisole and thioanisole. We describe herein the one-photon and two-photon photophysical properties of these chromophores, their photopolymerization efficiency as well as their applications, in particular in two-photon stereolithography. Of particular interest, we demonstrate a luminescence ON-OFF process controlled by quenching diffusion dynamics which can be modulated by the geometry and topology of the permeable 3D microstructures.



References

[1] C. Barner-Kowollik, M. Bastmeyer, E. Blasco, G. Delaittre, P. Müller, B. Richter, M. Wegener, *Angew. Chem. Int. Ed*, **2017**, *56*, 15828-15845.

[2] M. Pawlicki, H. A. Collins, R. G. Denning and H. L. Anderson, *Angew. Chem. Int. Ed.*, **2009**, *48*, 3244-3266.

[3] R. Zhou, J.-P. Malval, M. Jin, A. Spangenberg, H. Pan, D. Wan, F. Morlet-Savary, S. Knopf, *Chem. Comm.* **2019**, *55*, 6233-6236.

[4] N. Durand, R. Mhanna, P. Savel, H. Akdas-Kilig, J.-P. Malval, O. Soppera, J.-L. Fillaut, *Chem. Comm.* **2020**, *56*, 12801-12804.

[5] R. Zhou, R. Mhanna, M. Jin, H. Pan, D. Wan, D.-L. Versace, C. Thomas, F. Morlet-Savary, O. Soppera, J.-P. Malval, *ACS Appl. Polym. Mater.*, **2021**, *3, (6)*, 3103–3113.

[6] R. Mhanna, R. Zhou, M. Jin, H. Pan, D. Wan, D.-L. Versace, N. Hobeika, A. Khitous, O. Soppera, P. Lamielle, J.-P. Malval, *J. Mater. Chem. C*, **2022**,*10*, 11983-11994.

OC 18

INSIGHTS FROM COMPUTATIONAL MODELING ON THE SINGLET-TRIPLET CONVERSION IN MR-TADF AND INVERT SINGLET-TRIPLET GAP MATERIALS

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Keywords: OLEDs, TADF emitters, computational chemistry

Thermally Activated Delayed Fluorescence (TADF) process has appeared as the most popular design strategy towards reaching 100% internal quantum efficiency for Organic Light-Emitting Diodes (OLEDs). TADF consists in promoting upconversion of triplet excited states into emissive singlet ones through Reverse InterSystem Crossing (RISC), a process driven by spin-orbit coupling (SOC) and requiring a small singlet-triplet gap ΔE_{ST}. The advancement of the TADF field occurred essentially through materials design, the first strategy, as proposed by C. Adachi and co, consisting in connecting electron donating and accepting units to decrease the ΔE_{ST}. However, in doing so, the lower-lying singlet and triplet excited states bear a dominant charge transfer character that translates into a broad emission spectrum.

In this contribution, we will discuss based on computational considerations how doped triangle-shaped molecules can lead to (i) concomitant narrow emission, high quantum yield of emission and small ΔE_{ST} resulting in a whole new generation of TADF emitters, the multi-resonant TADF emitters[1] and to (ii) a new family of compounds with an inverted singlet-triplet gap and potentially, a downwards energy RISC.[2,3] To do so, we rely on high level quantum chemical calculations and show that an accurate description of electron correlation effects is key to correctly predict the excited states ordering as well as the optical properties of these compounds.[4]

[1] A. Pershin, D. Hall, V. Lemaur, J.C. Sancho-Garcia, L. Muccioli, E. Zysman-Colman, D. Beljonne, and Y. Olivier, Nat. Commun. **2019**, 10. 597.
[2] G. Ricci, E. San-Fabián, Y. Olivier, J. C. Sancho-García, ChemPhysChem **2021**, 22. 553.
[3] J. Sanz-Rodrigo, G. Ricci, Y. Olivier, J. C. Sancho-García, J. Phys. Chem. A. **2021**, 125. 513.
[4] G. Ricci, J. C. Sancho-García, Y. Olivier, J. Mater. Chem. C **2022**, 10. 12680.

OC 19

QM/MM calculations and spectra modelling of the bioluminescent system NanolucFurimamide

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Keywords: Bioluminescence; Force Field; Molecular Dynamics; QMMM; Absorption Spectra

Bioluminescence is a biological phenomenon of light production by living species with many applications[1], notably for the detection of cancer cells[2].The present study deals with a ligand-protein system (furimazine – Nanoluciferase) derived from a shrimp called *Oplophorus gracilirostri* with a very high luminescence intensity[3]. The protein catalyzes an oxidation reaction of furimazine by dioxygen, which leads to a new molecule, furimamide in its excited state. A better understanding of this system will provide insights to tailor new devices with emission of a photon with a red color, and thus a light signal more easily detectable inside the human body.

Simulations of the emission and absorption spectra are relevant tools[4] to comply this goal. We focus here on the absorption spectra of the light emitter system furimamide – Nanoluciferase. In order to take into account the protein environment and the system flexibility, we carry out classical molecular dynamics (MM) with AMBER software. Furimamide is a flexible molecule: standard force fields such as GAFF[5] (General Amber Force Field) are unable to reproduce correctly torsion angles potential energy when compared to in vacuo DFT computations. Thus, we perform a multidimensional fit using 1D and 2D potential energy surface scans with several torsion angles of the molecule in order to parameterize a new force field. Then, we compute electronic transitions at a QM/MM level of theory on a set of 100 snapshots extracted from each MM trajectory. We present analysis of the most important transitions and influence of the cavity. As a perspective, we plan to use the same methodology to simulate emission spectra.

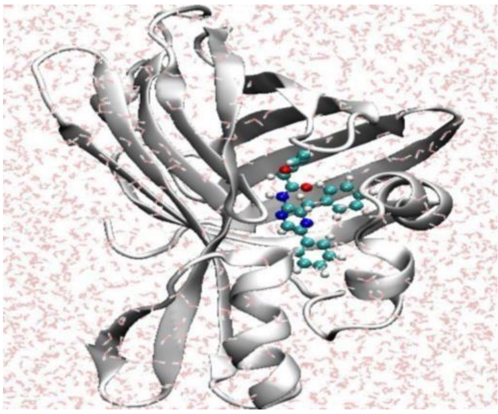

Figure 1. Ligand furimamide (colored molecule) inside the cavity of Nanoluciferase protein (in grey). The system is solvated inside a truncated octahedron water box.

[1] A. J. Syed et J. C. Anderson, *Chem. Soc. Rev.* 50 **2021** 5668-5705.

[2] M. A. Paley et J. A. Prescher, *Medchemcomm* 5 **2014** 255-267.

[3] M. P. Hall *et al.*, *ACS Chem. Biol.*, 7 **2012** 1848-1857.

[4] M. Sahihi, J. Sanz García, et I. Navizet, *J. Phys. Chem. B* 124 **2020** 2539-2548.

[5] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, et D. A. Case, *Journal of Computational Chemistry* 25 **2014** 18.

OC 20

MOLECULAR LIGHT-TO-HEAT CONVERTERS: A NEW STRATEGY FOR AN OLD PROBLEM

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Keywords: molecular heaters, excited states dynamics, photothermal, computational photochemistry

One major challenge in the twenty-first century is to increase global food production while the quality and quantity of arable land are diminishing. Central to this problem is the necessity to increase the yield of numerous important crop species and to find ways to extend geographical locations suitable for agriculture. One environmental constraint which hinders plant growth and development is cold stress. To protect plants from cold stress, we propose the use of molecular heaters, molecules which can absorb light at specific wavelengths and convert it into heat. Combining efforts from synthesis, spectroscopy, toxicology, and computational calculations, we present a series of suitable candidates to be used as molecular heaters.[1-3] Particularly, we use different quantum chemical approaches such as TDDFT, DFT/MRCI, CASSCF/CASPT2, and surface hopping simulations to elucidate the photodeactivation mechanism of these molecules. Our target chromophores are inspired by sinapoyl malate (SM), a naturally occurring molecule identified as an efficient photoprotective plant sunscreen.[4] Our SM derivatives present a fast and efficient relaxation mechanism that involves population transfer from an initially populated bright ^{1}□□* state to a dark twisted charge transfer (TICT) state. This intermediate state is formed after a carbon-carbon double bond rotation and mediates an efficient internal conversion to the ground state through a conical intersection. The photoisomer formation is naturally prevented due to a symmetric substitution in one of the sp^2 carbons, ensuring almost complete recovery of the initial ground state. In summary, we present a class of nature-inspired molecules with an efficient nonradiative energy dissipation mechanism allowing the absorbed light to be converted into heat with minimal implication for photosynthesis. Considering their green synthesis, impressive photostability, and lack of critical toxicity, these molecules are promising molecular heaters for applications in agriculture, phototherapy, and generally where photothermal conversion is desirable.

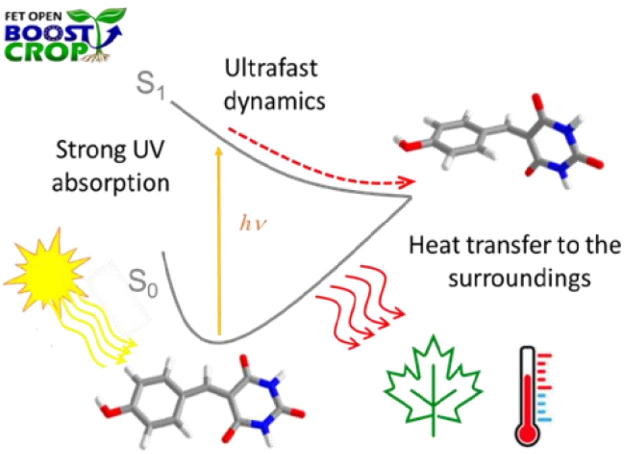

Figure 1. Schematic representation of the photophysics of molecular heaters.

[1] Abiola, T. T.; Toldo, J. M.; Barbatti, M.; Allais, F.; Stavros, V. *et al. J. Phys. Chem. Lett.* **2021,** *12***,** 337.
[2] Toldo, J. M.; do Casal, M. T.; Barbatti, M. *J. Phys. Chem. A* **2021**,*125*, 5499.
[3] Abiola, T.T.; Toldo, J. M.; Barbatti, M.; Stavros, V.; Allais, F. *et al. Chem. Sci.* **2021**, *12*, 15239.
[4] Baker, L. A.; Allais, F.; Stavros, V. *et al*. *Chem. Phys. Chem*. **2020**, *21*, 2006.

OC 21

A Supramolecular Nanoassembly of Lenvatinib and a Green Light-Activatable NO Releaser for Combined Chemo-Phototherapy

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Keywords: Light; Nitric Oxide; Chemotherapy; Cyclodextrin Polymers; Lenvatinib; Combination therapy

In the last years, the combination between conventional chemotherapeutics with unconventional anticancer agents has received increasing attention. The final goal is to potentiate the therapeutic outcome due to additive/synergistic effects while minimizing the side-effects typical for chemodrugs.[1]. Among the “unconventional therapeutics”, nitric oxide (NO) is very appealing. However, the biological effects of this free radical in cancer are strictly depending on its site of generation and doses. Therefore, light-activatable NO photodonors (NOPDs) are more intriguing than spontaneous NO releasers due to the very precise spatio-temporal control they offer.[2] Recently we have reported a combination of a polymeric blue light-activatable NO releaser with the chemotherapeutic Sorafenib.[3] In this contribution, we report an improvement of this work proposing a supramolecular nanoassembly based on a watersoluble cyclodextrins polymer and co-encapsulating a red fluorescent NO releaser activatable with the more biocompatible green-light and the chemotehrapeutic Lenvatinib, an antitumoral largely administered for hepatocellular and differentiated thyroid carcinoma treatment. The photophysical and photochemical properties of this novel macromolecular construct are illustrated and the biological tests on tumoral cell lines are reported.

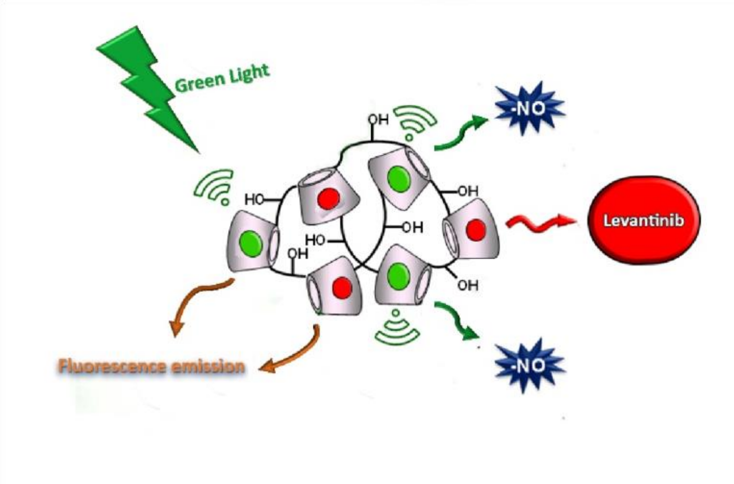

Fig. 1. *Schematic representation of the supramolecular construct.*

References:

[1] A. Fraix, N. Marino, S. Sortino, Phototherapeutic Release of Nitric Oxide with Engineered Nanoconstructs. in *Top Curr Chem*., Springer, **2016**, 370:22557.

[2] S. Sortino, Photoactivated nanomaterials for biomedical release applications. *J Mater Chem*. **2011**, 22, 301-318.

[3] F. Laneri, ACE Graziano, M. Seggio, A. Fraix, S. Sortino et al. Enhancing the Anticancer Activity of Sorafenib through Its Combination with a Nitric Oxide Photodelivering & β-Cyclodextrin Polymer. *Molecules*. **2022,** 27. 1918.

OC 22

TUNING THE PHOTOPHYSICS OF ITQ-51 ZEOTYPIC STRUCTURE

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Keywords: hybrid structures, fluorescence, zeotypes, crystallization inclusion method, artificial antennas, FRET…

The results presented in this work demonstrate the feasibility of occluding dyes into restricted nanocavities of zeotypic materials to promote new and/or enhanced photophysical processes in organic fluorophores. 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, which will determine the final emissive properties of the photoactive material and, therefore, its best field of application. 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.

Therefore, as the host framework, a Mg-doped ITQ-51 zeotype [1] with an extra-large pore opening of 9.3 Å x 10.6 Å has been selected. In particular, this framework has blue fluorescent properties and has been synthesized without the need to incorporate additional dyes into the synthesis gel, due to the intrinsic emissive characteristics of the template (DMAN, Figure 1a) guiding the crystallization. In addition, it has been demonstrated that this material shows photophysical changes over time, due to the fact that the structure-directing organic agent (DMAN) employed for its crystallization exhibits a redistribution within the unidirectional IFO channels, favoring the formation towards thermodynamically more stable aggregates.

Based on this starting fluorescent zeotype (DMAN/ITQ-51), the fluorescence range of the material has been broadened by the simultaneous occlusion of different active guests by the *crystallization inclusion* method, giving rise to artificial antennas (an efficient method demonstrated in other previous works).[2] By combining suitable FRET dye pairs with properties in the green and red regions of the visible spectrum, such as R123 (Rhodamine 123) and NB (Nile Blue, Figure 1b-c), different emissive properties (green or red fluorescence) have been induced compared to the starting structure, allowing to develop possible efficient lasers in different areas of the spectrum. In these systems, the resultant fluorescence color emission is highly dependent on the probability of FRET processes between the simultaneously occluded dyes in the restricted space of the zeotype channels. Likewise, distribution, concentration and relative proportions of the dyes play a key role in improving FRET efficiency, and consequently influence the final emissive properties of the resultant material.

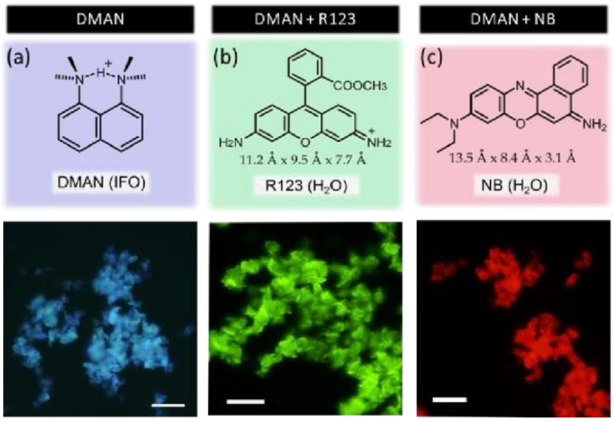

Figure 1. Selected molecular structures for energy transfer within Mg-doped ITQ-51 channels with their molecular dimensions (a) DMAN (structuredirecting agent), (b) Rhodamine 123 (R123), and (c) Nile Blue (NB), and the fluorescence image of the as-synthesized particles below. Scale =20 µm.

[1] Martínez-Franco, R.; Moliner, M.; Yun, Y.; Sun, J.; Wan, W.; Zou, X.; Corma, A. , Proceedings of the National Academy of Sciences, 2013, 110, 3749–3754. [2] aca . a e-a e . S la la . e -Arbeloa, I., & e -Pariente, J. , The Journal of Physical Chemistry C, 2013, 117(45), 24063-24070.

OC 23

Resin Additive for UV 3D printing resins with (Bio)degradable properties

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Keywords: ***3D printing, degradable materials, radical ring-opening polymerization, photopolymerization, microstructuring***

Three-dimensional (3D) printing and especially VAT photopolymerization leads to highly cross-linked materials with high thermal, chemical and mechanical properties. Nevertheless, such stability is incompatible with degradability and re/upcyclability. A high volume of 3D-printed thermoset must be incinerated or stored in landfills following use, making this so promising manufacturing process not environment friendly or sustainable. In order to solve this problem, thionolactone and especially dibenzo[c,e]-oxepane-5-thione (DOT) was used as an additive (only 2wt%) to model acrylate-based resins. The principle is based on the introduction of heteroatoms (more specifically thioester linkage) into the network backbone via a radical ring-opening polymerization. These weak bonds confer (bio)degradability to the 3D-printed object. The low amount of additive allows to only slightly modify the printability of the resin, keep intact its resolution and maintain the mechanical properties of the 3D polymer object. The resins with additive were used in UV microfabrication setup, two-photon stereolithography setup and commercial 3D printers. The fabricated objects were shown to degrade in basic solvent under mild conditions as well in a home-made compost. The rate of degradation is nonetheless dependent of the size of the object. This feature was used to prepare 3D objects with support structures that could be easily solubilized, opening the door to the 3D printing of stacked objects in the z direction.

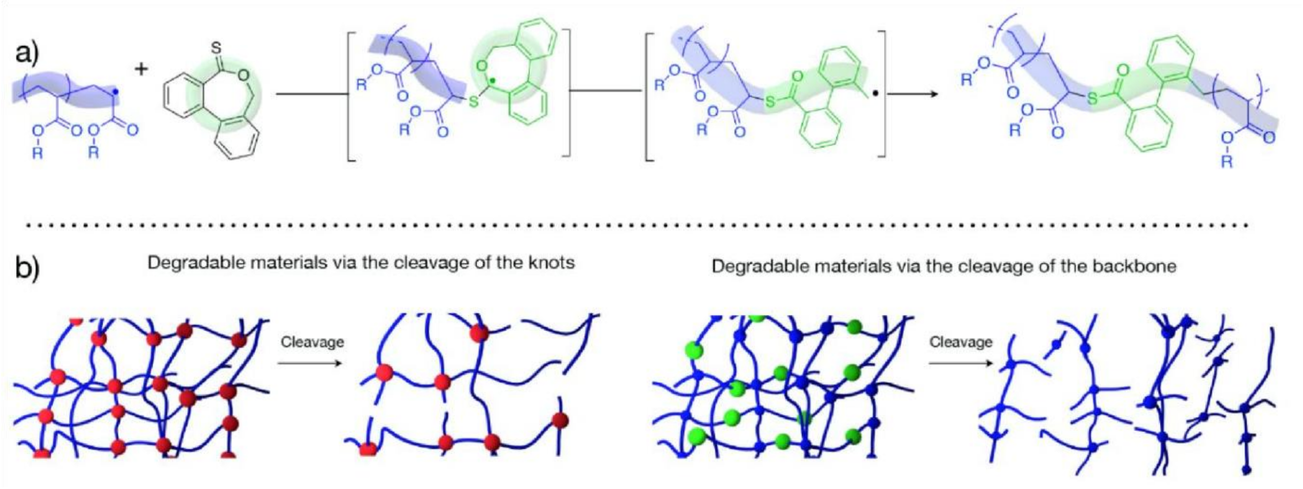

Figure 1. a) Polymerization mechanism involving the DOT/acrylate monomer pair b) Degradation illustration: knots cleavage and backbone cleavage. Both from [1].

[1] N.Gil, C.Thomas, R.Mhanna, J.Mauriello, R.Maury, B.Leuschel, J-P. Malval, J-L. Clément, D.Gigmes, C.Lefay, O.Soppera, Y.Guillaneuf Angewandte Chemie, **2022**, Volume 61, Issue 18.

OC 24

GUEST RELEASE FROM LIPOSOMES USING VISIBLE LIGHT

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Keywords: Liposomes, photochromic compounds, visible light, drug delivery

Liposomes are artificial vesicles that have emerged in recent years as vehicles to engineer functional membranes and to deliver molecules to cells.[1] In this work, light-responsive Donor-Acceptor Stenhouse Adducts (DASAs, figure 1a) have been incorporated within the bilayer membrane of liposomes.[2] The significant change of the physicochemical properties, including polarity, associated with the photoswitching process of these compounds was exploited to obtain controlled guest release from the membrane to the outside environment upon irradiation (figure 1b). Liposomes were functionalized with different DASAs, and the resulting vesicles were studied by dynamic light scattering and UV-vis spectroscopy, allowing to determine the encapsulation efficacy of each guest and the effect of the intercalation on the properties of the liposomes. In all cases, a spontaneous interconversion of the open form to the cyclized form was observed over time, which could be accelerated by visible light irradiation. The subsequent partitioning of the cyclized species was studied via size-exclusion chromatography, showing it is possible to obtain guest relocation from the membrane of the liposomes to the aqueous environment upon isomerization.

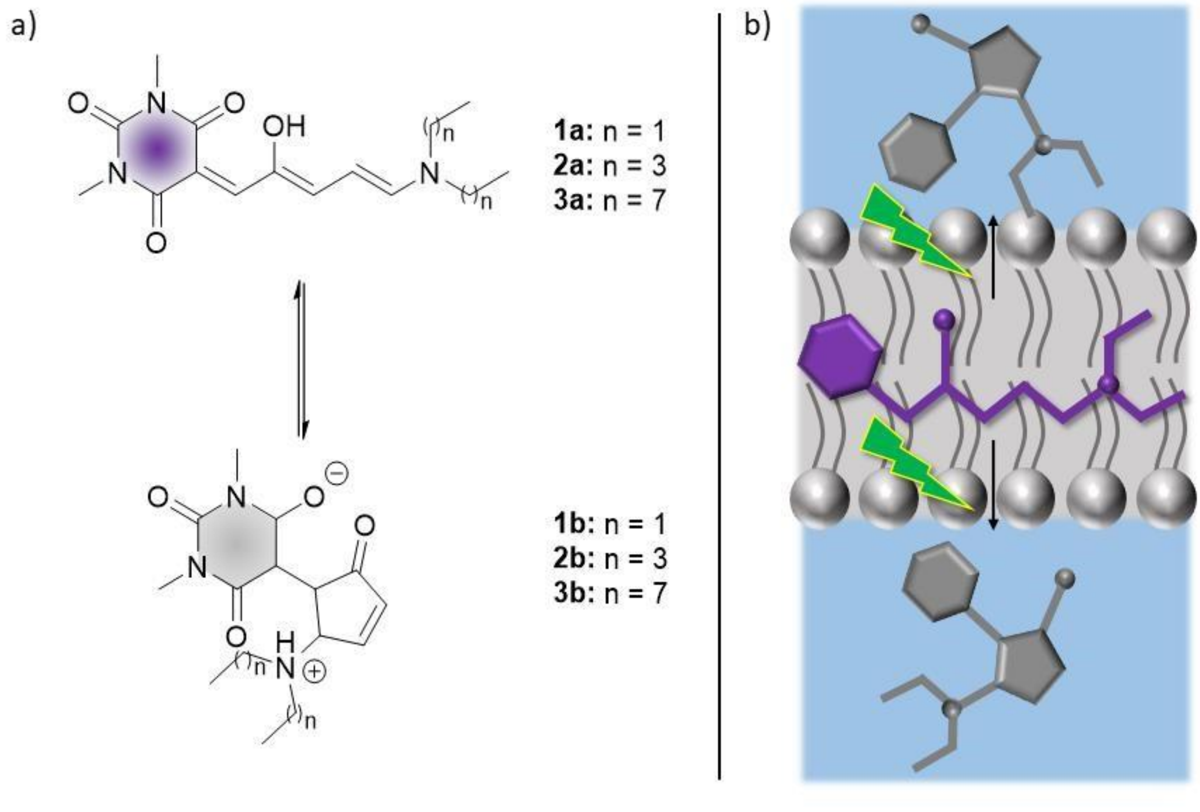

Figure 1. a) structures of the DASAs employed; b) schematics of DASAs relocation upon isomerization..

Financial support from the Italian Ministry of Education, University and Research MIUR (PRIN 201732PY3X) is gratefully acknowledged.

[1] M. J. Langton, *Nat. Rev. Chem.* **2021**, 5, 46-61.
[2] M. M. Lerch, W. Szymanski, B. Feringa, *Chem. Soc. Rev.* **2018**, *47*, 1910-1937.

OC 25

CLAY-BASED AND MESOPOROUS SILICA NANOPARTICLES AS CARRIERS FOR PHOTODYNAMIC THERAPY

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Keywords: photosensitizers; functionalized silica nanoparticles; folic acid; PEG; photodynamic therapy; HeLa cells; (photo)toxicity

Cancer is the second cause of human death worldwide and currently, the most common procedures against it are radiotherapy and chemotherapy. Nevertheless, both treatments damage healthy cells, and consequently, patients suffer important side effects. For that, in this work, photodynamic therapy (PDT) is proposed as a complementary cancer treatment. PDT is a minimally invasive procedure in which under suitable light irradiation a sensitive drug (photosensitizer, PS) is activated and generates Reactive Oxygen Species (ROS), mainly singlet oxygen ($^1O_2$), a cytotoxic species able to damage nearby cells. Nowadays, there are many different photosensitizers but most of them are not adequate for their use against tumors because of their poor aqueous solubility and their lack of selectivity for cancer tissues. Therefore, mesoporous silica nanoparticles (MSN) and clay-based nanoparticles are proposed as carriers for these PSs due to their excellent properties, good biocompatibility, tunable size, easy functionalization, high chemical stability, and optically transparent. [1]

In this research, these two different nanosystems were used, Laponite-clay (LAP) and Mesoporous Silica Nanoparticles (MSN), Figure 1. These carriers were decorated not only with commercial photosensitizer but also with other molecules of interest; polyethylene glycol (PEG) and folic acid (FA) to improve the stability of nanocarriers in aqueous media and the selectivity to cancer cells, respectively. [2] The final hybrid nanosystems with high singlet oxygen generation, good stability, and selectivity were tested *in vitro* in HeLa cells to demonstrate their photoactivity under specific irradiation and their viability to be used in PDT, Figure 1. [3]

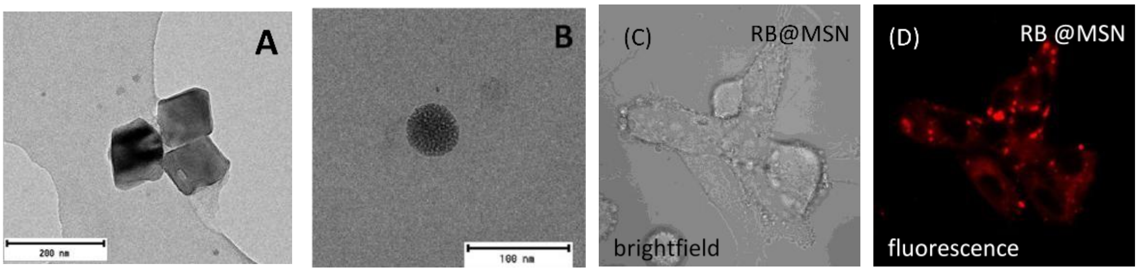

Figure 1. TEM image of LAP and MSN (A and B, scale bar 200 nm and 100 nm respectively) and fluorescence images of RB@MSNs in HeLa cells at 1 μg/mL (C and D scale bar 100 nm).

[1] SS. Lucky, KC. Soo, Y. Zhang. Chem. Rev. **2015**, 115, 1990-2042.
[2] R. Prieto-Montero, A. Katsumiti, *et al*. Sensors. **2020**, 20, 5590-5605
[3] R. Prieto-Montero, A. Prieto-Castañeda, *et al*., Int. J. Mol. Sci. **2021**,22, 6618-6641.

OC 26

Photo-control of G-quadruplex DNA folding

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Keywords: G-quadruplexes, photoswitches, time-resolved spectroscopy, circular dichroism

Guanine-rich DNA sequences can self-assemble in stacking of tetrads of guanines, which are called Gquadruplexes. They are highly polymorphic and their folding and unfolding dynamics have been shown to be involved in cell regulation.[1] Therefore controlling these mechanisms by light attracts a growing interest for potential applications in photo-pharmacology or DNA nanotechnology. [2] Photoswitches such as AZO (see figure below), [3,4] a derivative of azobenzene can be used to induce G-quadruplex folding dynamics. Hence we have been working on the characterization of AZO with small G-quadruplex forming sequences, with several techniques including UV-visible absorption, circular dichroism, NMR and femtosecond transient absorption. We then begun a time-resolved circular dichroism study of the system over a window ranging from femtoseconds to seconds. [5]

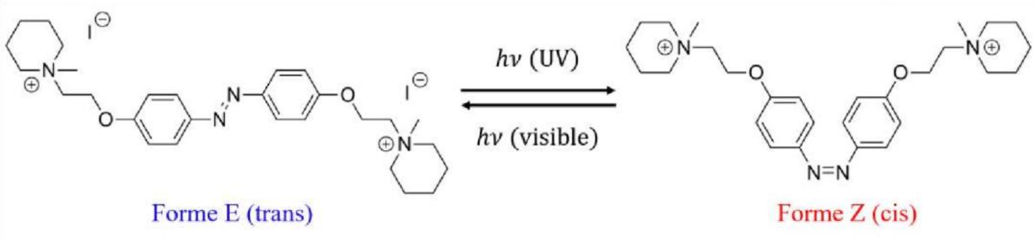

Figure 1. Photoswitch AZO.

[1] The regulation and functions of DNA and RNA G-quadruplexes. Varshney, D.; Spiegel, J.; Zyner, K.; Tannahill, D.; Balasubramanian,S. Nat Rev Mol Cell Bio, 2020, 21, 459-474.

[2] Photoresponsive Control of G-Quadruplex DNA Systems. Ramos-Soriano J. and Galan M. C., JACS Au 2021, 1, 1516-1526

[3] Reversible Photoswitching of a G-Quadruplex. Ogasawara, S.; Maeda, M. Angew. Chem. Int. Ed. 2009, 48 (36), 6671-6674.

[4] Conformational Switching of G-Quadruplex DNA by Photoregulation. Wang, X.; Huang, J.; Zhou, Y.; Yan, S.; Weng, X.; Wu, X.; Deng, M.; Zhou, X. Angew. Chem. Int. Ed. 2010, 49 (31), 5305-5309.

[5] Multiscale conformational dynamics probed by time-resolved circular dichroism from seconds to picoseconds. Hache, F.; Changenet, P. Chirality 2021, 33 (11), 747-757.

OC 27

BrightSwitch®: A New Family of Dual Emissive Photoconvertible Fluorescent Probes for Bioimaging

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Keywords: Fluorescence, Bioimaging, super-resolution imaging

Photoconversion is a powerful tool in bioimaging for tracking organelles and biomolecules in cells and can advantageously be used in SMLM. Although photoconvertible proteins dominate the field, small molecular photoconvertible probes that present advantages over proteins remain rare. [1-2] Herein we present BrightSwitch®: a new family of dual emissive photoconvertible fluorescent probes. The BrightSwitch® probes are based on bright fluorophores like coumarins and BODIPYs conjugated to an ASORM (Aromatic singlet oxygen reactive moiety). Upon excitation, the fluorophore generates singlet oxygen, which selectively oxidizes the ASORM and leads to an hypsochromic shifts in absorbance and emission spectra. This mechanism that we established is called Directed Photooxydation Induced Conversion (DPIC). In addition, these probes display blinking properties without any specific buffer and thus can be used as probes for SMLM in live cells. These probes were designed to fit with typical microscope channels and are adapted to excitation sources like 405, 488, 560 and 640 nm. Owning to their functionalization site, the BrightSwitch® can be targeted to various organelles (plasma membrane, mitochondria, actin, etc.) and can be tagged to proteins (SNAP, Halo, etc) offering a versatile tool for organelles and biomolecules tracking and imaging in advanced microscopy.

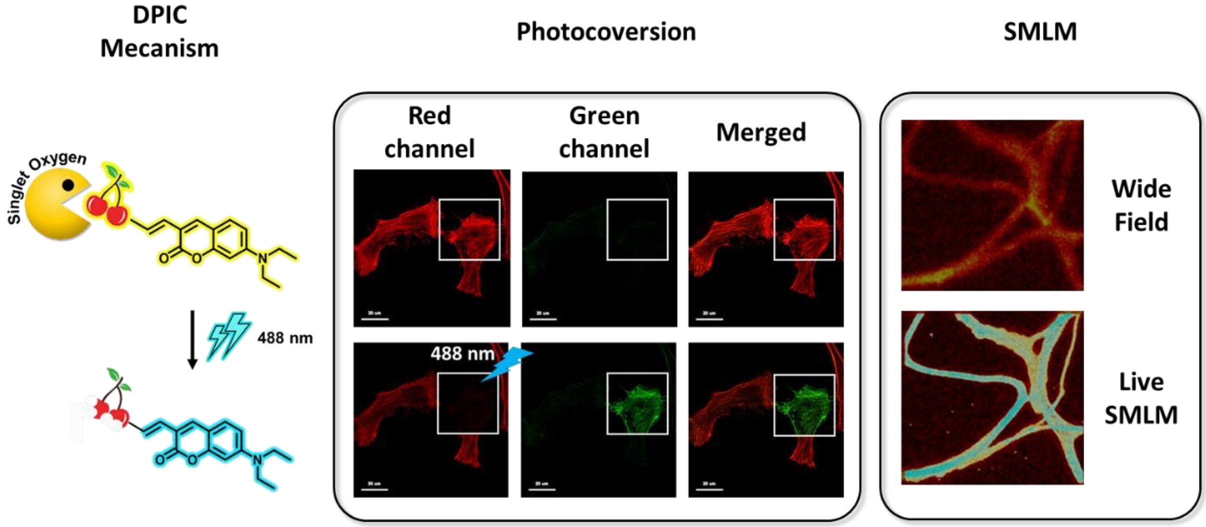

Figure. *Properties of BrightSwitch® dyes and their applications in fluorescence imaging*

Acknowledgments: This work was supported by the French National Research Agency (ANR) grant BrightSwitch 19-CE29-0005-01.

References: [1] Jun, et al. *J. Am. Chem. Soc.* **2019**, *141* (5), 1893–1897. [2] Cho et al. *J. Am. Chem. Soc.* **2021**.

OC 28

A novel molecular dyad for combined PDT and NO-PDT in cancer cells

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Keywords: Photodynamic therapy, Nitric oxide, Light, Multimodal therapy, Polymer nanoparticles

Photodynamic therapy (PDT) is a well-known therapeutic modality based on the photocontrolled generation of the highly reactive singlet oxygen ($^1O_2$) for the treatment of malignant lesions like cancer[1]. Combination of PDT with other unconventional therapeutic species is emerging as a promising strategy which aims at exploiting the additive/synergistic effects arising from multiple species in order to increase the effectiveness of therapeutic treatment and to minimize side effects[2]. On this regard, the coupling of PDT photosensitizers (PSs) with nitric oxide photodonors (NOPDs) is opening new perspective. Molecular dyads integrating within the same molecular skeleton PSs and NOPDs are of great interest because offer the advantage to photorelease $^1O_2$ and NO in the "same region of space". However, the design of such systems is a difficult task since the generation of comparable amounts of $^1O_2$ and NO is necessary in order to observe the desired improved photodynamic effects but $^1O_2$ quantum yields (Φ_Δ) of many PSs are often much larger than those of NO (Φ_{NO}) of organic NOPDs[2]. Herein we present the design, photochemical properties and biological evaluation of a novel molecular dyad integrating a PS and a NOPD within the same skeleton (Figure 1) and generating, under activation with visible light, $^1O_2$ and NO with comparable quantum yields[3]. Besides, the non-fluorescent NOPD unit becomes highly fluorescent after the NO release, acting as an optical reporter for the NO photogenerated. The dyad is not soluble in water but is effectively entrapped in water-dispersible, biodegradable polymeric NPs made of mPEG-PCL. The NPs effectively deliver the dyad into the cytoplasm of HepG2 hepatocellular carcinoma cells. A remarkable decrease of cell viability is observed for the loaded NPs using very low concentrations of the dyad and very low light doses, as result of the combined photodynamic action of $^1O_2$ and NO. These properties make this dyad a very appealing candidate for further biomedical studies.

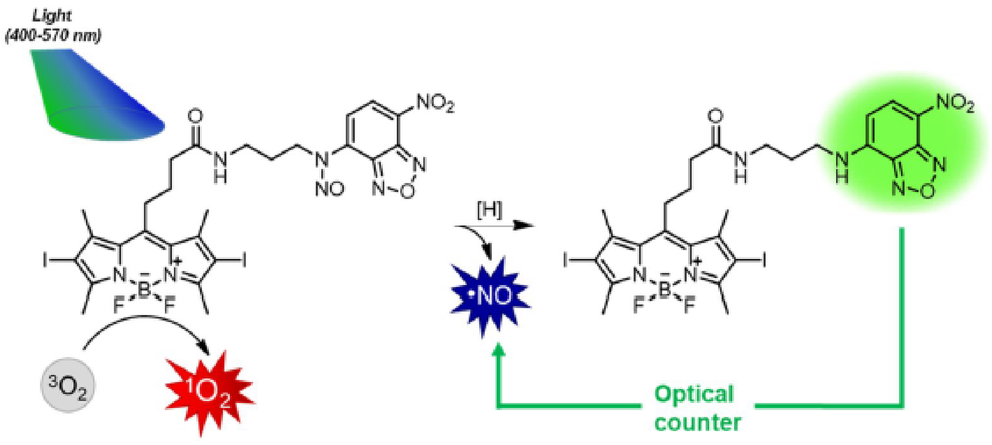

Figure 1. Structure of the molecular dyad photogenerating $^1O_2$, NO and a stable photoproduct under visible light.

[1] M. R. Hamblin, T. Hasan, Photochemical and Photobiological Sciences, **2004**, 3, 436-450.
[2] A. Fraix, S. Sortino, Photochemical and Photobiological Sciences, **2018**, 17, 1709-1727.
[3] C. Parisi, G. Longobardi, A.C.E. Graziano, A. Fraix, C. Conte, F. Quaglia, S.Sortino, Bioorganic Chemistry, **2022**, 128, 106050.

OC 29

A Multiresponsive Calix[6]arene Pseudorotaxane Empowered by Fluorophoric Dansyl Groups

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Keywords: supramolecular chemistry, pseudorotaxanes, molecular machines, calix[6]arene, dansyl unit

In the last two decades, calix[6]arenes have emerged as prominent hosts to devise pseudorotaxanes and mechanically interlocked molecules, due to their versatility and remarkable binding properties.[1] We report the investigation of a novel dansyl calix[6]arene and of its pseudorotaxane complex with a bipyridinium-based axle (Figure 1). In analogy with parent compounds,[2] the macrocycle shows a strong affinity towards the bipyridinium and their complex can be disassembled upon reduction of the latter. At the same time, the three dansyl units add new and emerging features to the complex, allowing to: i) signal the state of the system by fluorescence (which is quenched upon association); ii) lower the complexation ability of the host by protonation of the dansyl units; iii) enable photoinduced electron transfer processes, which can be exploited to reduce the guest and therefore disassemble the complex. Overall, the investigated pseudorotaxane is a multiresponsive system which can be controlled by means of three reversible and orthogonal stimuli: the reduction of the guest (electrochemical stimulus), the protonation of the host (chemical stimulus) and the photoinduced reduction of the guest *via* the host (light stimulus).

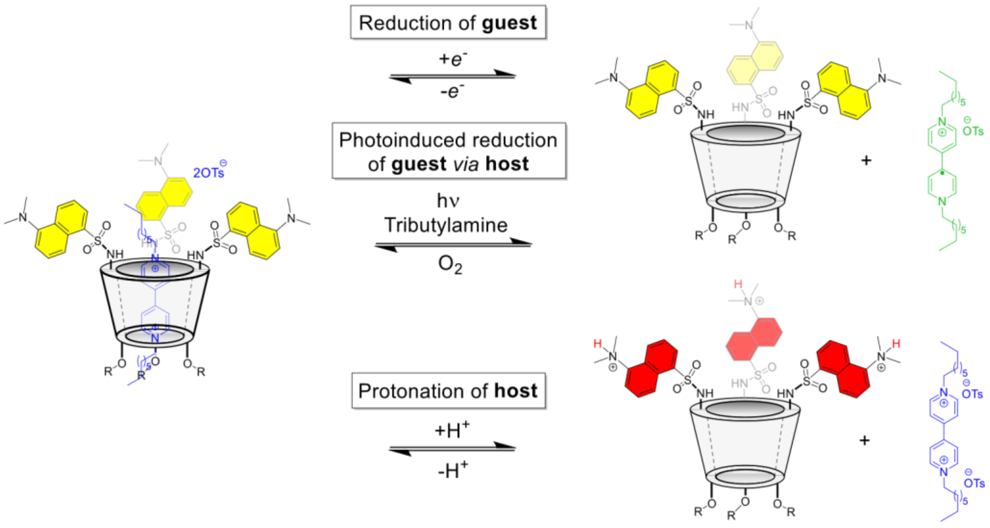

Figure 1. Schematic representation of the calix[6]arene-based pseudorotaxane and its responsiveness to different stimuli.

[1] G. Cera, A. Arduini, A. Secchi, A. Credi, S. Silvi, Chem. Rec. **2021**, 21, 1.
[2] A. Credi, S. Dumas, S. Silvi, M. Venturi, A. Arduini, A. Pochini, A. Secchi, J. Org. Chem. **2004**, 69, 5881.

This work was supported by the Italian MUR (PRIN 20173L7W8K).

OC 30

Development of Superoxide Anion Sensing Compounds based on Chemiluminescent Coelenterazine

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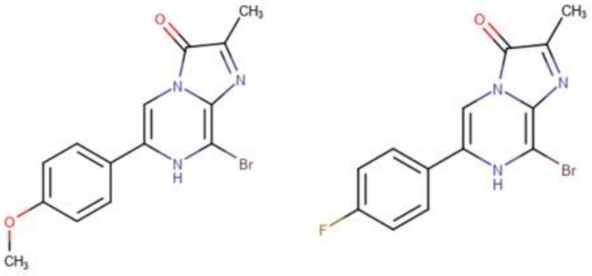
Keywords: Superoxide Anion, Cancer, Sensing Probe, Chemiluminescence, Coelenterazine

Superoxide anion corresponds to a reactive oxygen species that acts as a signaling molecule within the organism, being that, in cases of pathologies, such as cancer, this species can be overexpressed, acting as a specific marker of the disease [1]. Considering this, it became of high priority to develop methods capable of detecting superoxide anion level variations with high sensitivity and specificity.

One emerging approach is the use of chemiluminescent compounds, such as the widely studied marine coelenterazine, as sensing probes, which can emit light upon contact with the anionic species [2]. However, a significant restriction was noted in terms of the emission intensity, which is reduced in aqueous environments [3].

With this in mind, our research team developed and characterized two novel coelenterazine analogues, known as MeOBr-Cla and FBr-Cla, displayed in Figure 1, which presented a chemiluminescent reaction that was triggered by the presence of superoxide anion, with longer-lived light-emission intensity, in aqueous solutions of various pH levels, being remarkably superior to native Coelenterazine [4, 5]. Therefore, the new molecules showcase the potential to be employed as superoxide sensing probes with enhanced chemiluminescence.



MeOBr-Cla **FBr-Cla**

Figure 1. Schematic representations of the chemical structure associated to the novel coelenterazine analogues.

Acknowledgments: "*Fundação para a Ciência e Tecnologia*" (FCT) for funding of projects PTDC/QUI-QFI/2870/2020, UIDB/00081/2020 (CIQUP), LA/P/0056/2020 (IMS), as well as CEECINST/00069/2021 (L.P.d.S.).

References:

[1] Bronsart, L.L. et al. Molecular imaging and biology, **2016**, 18, (2), 166-171
[2] Pinto da Silva, L. et al. European Journal of Medicinal Chemistry, **2019**, 183, 111683
[3] Lourenço, J.M. et al. Journal of Luminescence, **2018**, 194, 139-145
[4] Silva, J.P. et al. Chemosensors, **2022**, 10, (5), 174
[5] Silva, J.P et al. Journal of Photochemistry and Photobiology A: Chemistry, **2023**, 434, 114228

OC 31

FROM NATURAL CHROMOPHORES TO ORGANIC DYES: EXPLORING THE CHEMISTRY OF *C*- AND *N*-SUBSTITUTED PHENAZINES

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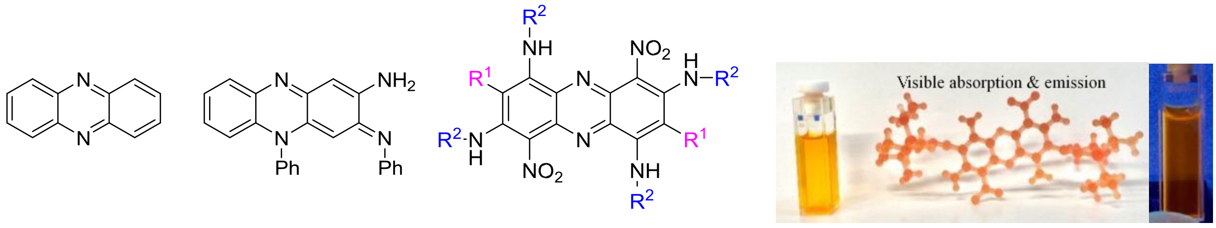
Keywords: phenazines, chromophores, organic dyes, aromaticity

With applications ranging from biology[1,2] to optoelectronics,[3] phenazine derivatives are solidly established as a family of chromophores worth investigating, from the point of view of the synthetic routes[1,4]. The particular backbone structure consisting of two aromatic rings fused to a pyrazine core, resulting in a stable, planar and a fully conjugated aromatic π-system renders these molecules with highly attractive and easily tunable features.

In the field of phenazine chemistry, numerous synthetic methodologies have been already developed and are being currently investigated to control the nature and position of the functional group which is dictating the desired properties. Successfully combining various key features into a final structure requires adapting or even establishing of a new design strategy.

During our study, we have developed an unexpected and straightforward methodology that allows the efficient synthesis of nitrogen- and carbon-substituted phenazines, the nature of the substituents being easily tunable. Moreover, the introduction of triisopropylsilyl (TIPS) group opens a way for further postfunctionalization via classic cross-coupling reactions. The obtained derivatives present attractive optical properties that could be further developed for organic electronics applications such as optical sensing or photovoltaics.



Phenazine Induline Tetra-aminophenazine

Figure 1: Phenazine structures and new substituted derivatives.

[1] J.B. Laursen and J. Nielsen, *Chem. Rev.* **2004,** *104*, 1663-1685.

[2] Z. Chen, S. Pascal, M. Daurat, L. Lichon, C. Nguyen, A. Godefroy, D. Durand, L. M. A. Ali, N. Bettache, M. Gary-Bobo, P. Arnoux, J.-F. Longevial, A. D'Aléo, G. Marchand, D. Jacquemin and O. Siri, *ACS Appl. Mater. Interfaces* **2021**, *13*, 30337−30349.

[3] X.-N. Qi, L.-R. Dang, W.-J. Qu, Y.-M. Zhang, H. Y., Q. Lin and T.-B. Wei, *J. Mater. Chem. C*, **2020**, *8*, 11308. [4] A. Chaudhary and J. M. Khurana, *Res. Chem. Intermed.*, **2018**, *44*, 1045–1083.

OC 32

LUMINESCENT TETRAHEDRAL AND OCTAHEDRAL MANGANESE(II) COMPLEXES WITH [O=P]-DONOR LIGANDS

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Keywords: manganese(II), [O=P]-donor ligands, luminescence

Luminescent Mn(II) complexes are of potential interest for lighting applications, for instance as replacement of expensive rare earths-based phosphors in fluorescent lamps [1]. The emission is related to the $^4T_1(G)\rightarrow{}^6A_1(^6S)$ transition and is strongly dependent upon the coordination geometry: tetrahedral complexes are normally green emitters, while octahedral species emit in the red range. However, the luminescent properties can be enhanced by the presence of rigid structures and light harvesting fragments, able to reduce the non-radiative decay and improve the absorption in the UV region [2].

On the basis of recent outcomes on dihalide derivatives with phosphine oxides, our research group exploited phosphoramides, arylphosphonic diamides, amidophosphates and phosphonates as ligands for the preparation of tetrahedral Mn(II) complexes having general formula $[MnX_2L_2]$ (X = Cl, Br, I). The complexes were isolated from the reaction between the proper anhydrous MnX_2 salt and L under mild conditions. The structure of the derivatives was ascertained by single-crystal X-ray diffraction. The species revealed to be appreciably luminescent in the green region upon excitation with UV-light, with emission maxima centered between 510 and 535 nm. The luminescence lifetimes are in the hundreds of μs range, strongly influenced by the choice of the coordinated halide. In general, the lifetime decreases passing from the chloro- to the bromo- and the iodo- derivative as a consequence of the increased spin-orbit coupling effect [3-5]. Instead, when 2-naphthyl or carbazolyl fragments were introduced in the skeleton of the [O=P]-donor ligands the corresponding tetrahedral Mn(II) complexes were characterized by dual emissions, with a band in the green region attributable to the metal center and another one, centered in the red region, ascribed to triplet states of the aromatic substituents [6-7]. Similar results were achieved with [O=P]-ligands based on P(III) such as dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (BPPO) and 9,10-dihydro-9-oxa-10phosphaphenantrene-10-oxide (DOPO) [8]. On the other hand, the coordination of Mn(II) to phosphonates containing the (R/S)-BINOL fragment determined an almost pure ^{3}LC emission with complete disappearance of the green band. Bidentate ligands prepared from DOPO allowed the isolation of the corresponding octahedral Mn(II) complexes characterized by intense emissions centered at 611 nm. Differently from tetrahedral derivatives the luminescent lifetimes are in tens of ms range for octahedral derivatives as the $^4T_1(G)\rightarrow{}^6A_1(^6S)$ transition is both parity and spin forbidden.

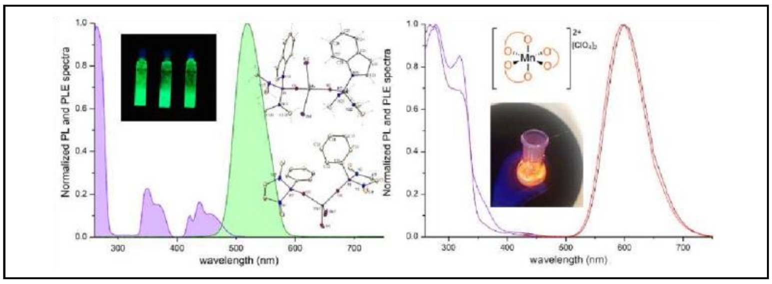

Figure 1. Green- and red-emitting Mn(II) complexes.

[1] K. Binnemans, P. T. Jones, J. Rare Earths, 2014, 32, 195.
[2] Y. Qin, P. She, X. Huang, W. Huang, Q. Zhao, Coord. Chem. Rev., 2020, 416, 213331.
[3] M. Bortoluzzi, J. Castro, A. Gobbo, V. Ferraro, L. Pietrobon, S. Antoniutti, New J. Chem., 2020, 44, 571.
[4] M. Bortoluzzi, J. Castro, A. Gobbo, V. Ferraro, L. Pietrobon, Dalton Trans., 2020, 49, 7525.
[5] M. Bortoluzzi, J. Castro, A. Di Vera, A. Palù, V. Ferraro, New J. Chem., 2021, 45, 12871.
[6] M. Bortoluzzi, V. Ferraro, J. Castro, Dalton Trans., 2021, 50, 3132.
[7] M. Bortoluzzi, J. Castro, V. Ferraro, Inorg. Chim. Acta, 2022, 536, 120896.
[8] V. Ferraro, J. Castro, L. Agostinis, M. Bortoluzzi, Inorg. Chim. Acta, 2023, 545, 121285.

OC 33

Non-reversible Photoinduced Phase Transition in the RbMnFe Prussian Blue Analogue Studied by Streaming Crystallography

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Keywords: ultrafast dynamics, photo-induced phase transition, Prussian blue analogue, time-resolved crystallography

Modern ultrafast laser technologies have opened new perspectives in controlling bistable magnetic materials, where light can be used to switch between different phases and thus different properties down to ultrashort timescales [1]. Among the available bistable materials, Prussian Blue Analogues (PBAs) are cyano-bridged bimetallic compounds with a phase transition based on a charge transfer between two stable states of different spin [2]. Moreover, the electronic charge transfer is coupled to symmetry breaking and large volume change, leading to a wide bistability hysteresis [3].

In this work, we followed the multiscale dynamics of the photoinduced phase transition within the thermal hysteresis of RbMnFe PBA micro-crystals (Figure 1) [4,5]. This was made possible by developing a new streaming crystallography method for time-resolved X-ray diffraction studies of non-reversible phenomena. Our results reveal that, above threshold excitation, complete photo-transformation from tetragonal to cubic phases can be achieved down to ultrashort timescales, leading to a permanent photo-induced phase. The out-of-equilibrium and multiscale dynamical behavior results from the coupling of volume strain driven by photoinduced charge transfer and symmetry change [5,6]. More generally, these results open a broad field of dynamical studies for photo-switching in bistable materials through ultrafast crystallography.

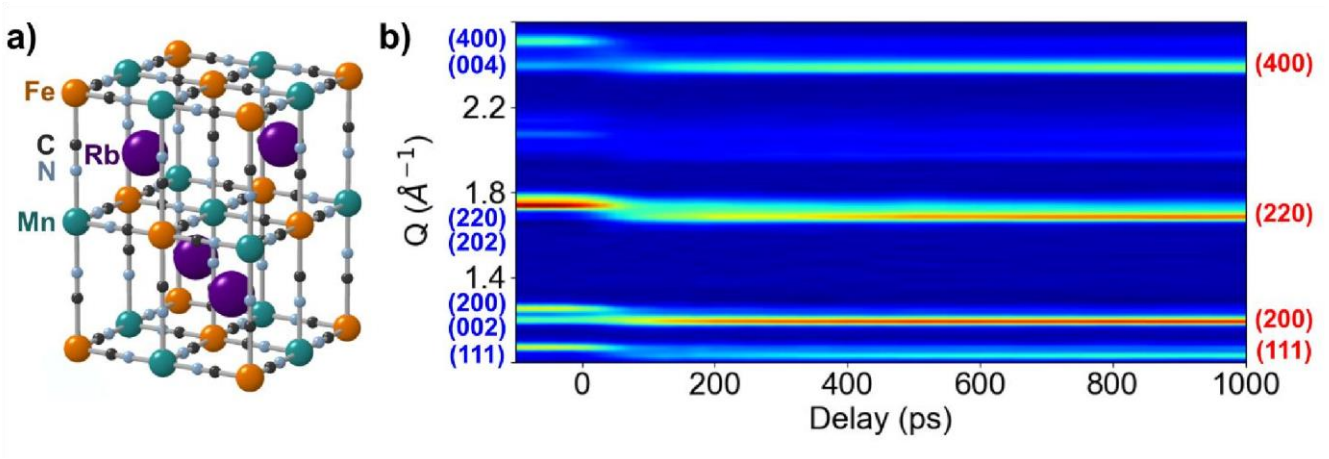

Figure 1. a) Structure of the RbMnFe PBA; b) Time-resolved X-ray diffraction pattern of RbMnFe, with (hkl) indices for the initial, tetragonal (left, in blue) and final, cubic (right, in red) phases.

[1] O. Sato, Nat. Chem., 2016, 8 (7), 644-656.
[2] H. Tokoro et al., Chem. Mater., **2008**, 20, 423-428.
[3] G. Azzolina et al., Phys. Rev. B, **2020**, 102, 134104.
[4] G. Azzolina et al., Eur. J. Inorg. Chem., **2019**, 2019, 3142-3147.
[5] G. Azzolina et al., J. Mater. Chem. C, **2021**, 9, 6773. [6] M. Hervé et al., in preparation.

Flash Communications

FC 01

INVESTIGATION INTO THE PHOTOPHYSICAL PROPERTIES OF HALOGENATED COELENTERAMIDE ANALOGS

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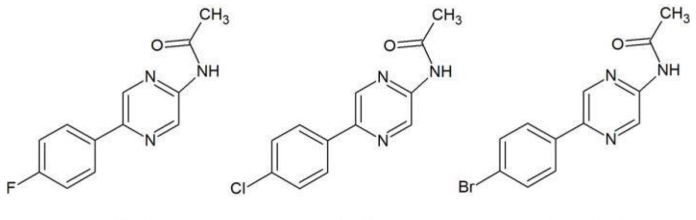
Keywords: Chemiluminescence; Bioluminescence; Coelenterazine; Coelenteramide; Photophysics; Microenvironment Probe

Among the most well-known chemi-/bioluminescent (CL/BL) system is marine Coelenterazine, in which Coelenteramide (Clmd) is generated and chemiexcited to singlet excited states, leading to light emission [1]. Due to this feature and its applicability in biologic media, CL/BL systems have been gaining practical applications in biomedical fields, like bioimaging and cancer therapy, among others [1–3].

Previous work performed by our group revealed that bromination of components of the Coelenterazine system provides them with enhanced and new properties (such as anticancer activity and enhanced emission) [2,4]. Given this, and knowing the role of Clmd in CL/BL reactions [4], this work aims to evaluate the photophysical properties of a brominated Clmd analog (Br-Clmd) (Figure 1) via UV-Vis and fluorescence spectroscopy [4]. Two novel fluorinated and chlorinated Clmd analogs, F- and Cl-Clmd (Figure 1), were also synthesized and characterized to further evaluate if changes are indeed due to Br, and not due to more general halogen-based effects.

The obtained UV-Vis and fluorescence spectra of the compounds were quite similar in aqueous solution, with absorption and emission at ~320 and 385 nm, respectively, which indicates that their emission is blue-shifted to that of native Clmd. Furthermore, the fluorescence quantum yield of the analogues in aqueous solution increases in the order of Br < Cl < F, which can be correlated with the heavy-atom effect. In particular, the fluorescence quantum yield of Br-Clmd displayed significant sensitivity to changes in solvent, revealing its potential use as a microenvironment fluorescence probe.



F-Clmd **Cl-Clmd** **Br-Clmd**

Figure 1. Chemical structures of the halogenated Clmds (F-, Cl- and Br-Clmd).

[1] Magalhães, C.M.; Esteves da Silva, J.C.G.; Pinto da Silva, L. ChemPhysChem, **2016**, 2286–2294.

[2] Magalhães, C.M.; González-Berdullas, P.; Duarte, D.; Correia, A.S.; Rodríguez-Borges, J.E.; Vale, N.; Esteves da Silva, J.C.G.; Pinto da Silva, L. Biomedicines, **2021**, *9*.

[3] Yan, Y.; Shi, P.; Song, W.; Bi, S. Theranostics, **2019**, *9*, 4047–4065.

[4] González-Berdullas, P.; Pereira, R.B.; Teixeira, C.; Silva, J.P.; Magalhães, C.M.; Rodríguez-Borges, J.E.; Pereira, D.M.; Esteves da Silva, J.C.G.; Pinto da Silva, L. International Journal of Molecular Sciences, **2022**, *23*.

FC 02

A theoretical study on DNA damage by chemiexcitation

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Keywords: dark photochemistry, DNA damage

Electronic excited states are present in many biological processes such as vison and photosynthesis. In these processes, the excited molecules are formed by photon absorption. However, other processes such as bioluminescence involve electronically excited molecules that are formed by a chemical reaction (chemiexcitation)[1]. Recently, this phenomenon has been linked to the formation of cyclobutane pyrimidine dimers (CPD) in DNA[2]. CPDs are a type of DNA damage that can lead to melanoma development if not repaired. Other diseases such as deafness or Parkinson's disease have also been related to chemiexcitation[3]. One of the sources of chemiexcitation processes is the breaking of a dioxetane ring. In the case of melanoma, the dioxetane is formed by the reaction of a melanin monomer, 5,6-dihydroxyindole-2-carboxylic acid (DHICA), with reactive oxygen species. However other biomolecules with indole moieties could be involved in chemiexcitation processes (Figure 1). In this work, several of these molecules have been studied to determine whether they could take part in chemiexcitation processes or not.

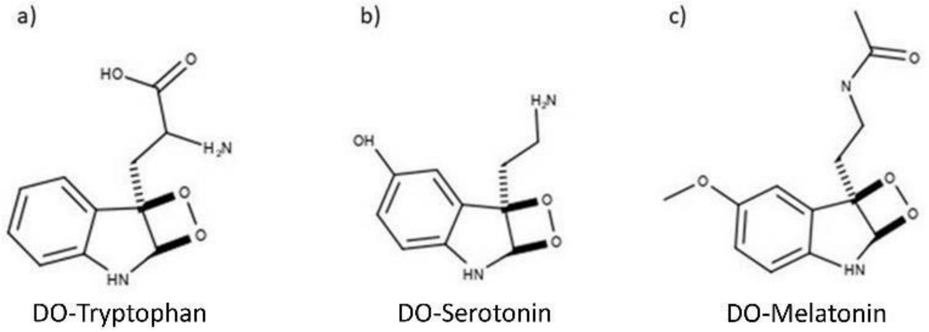

Figure 1. Three of the biomolecules that have been studied: the dioxetane derivative of tryptophan (DO-Tryptophan, a), serotonin (DO-Serotonin, b) and melatonin (DO-Melatonin, c).

Firstly, the decomposition reaction of the dioxetane derivative of DHICA (DO-DHICA) was studied. The decomposition reaction of DO-DHICA is a two-step reaction that happens through a diradical intermediate. This mechanism was used as a reference for the other molecules. The slow step of the reaction, the breaking of the O-O bond, was replicated in all the other studied dioxetanes and the results were compared to those of DO-DHICA. That way, the molecules with a kinetical behavior similar to DHICA could be identified. It was found that tryptophan, an essential amino acid, was one of these molecules. While further research is needed, these results show that under oxidative stress even biologically essential molecules could behave in an undesired way and could also be involved in some diseases whose origin is still unknown.

References

[1] Vacher, M.; Fdez Galván, I.; Ding, B.-W.; Schramm, S.; Berraud-Pache, R.; Naumov, P.; Ferré, N.; Liu, Y.-J.; Navizet, I.; Roca-Sanjuán, D.; Baader, W. J.; Lindh, R. *Chem Rev* **2018**, *118* (15), 6927–6974.

[2] Premi, S.; Wallisch, S.; Mano, C. M.; Weiner, A. B.; Bacchiocchi, A.; Wakamatsu, K.; Bechara, E. J. H.; Halaban, R.; Douki, T.; Brash, D. E. *Science* **2015**, *347* (6224), 842–847.

[3] Brash, D. E.; Goncalves, L. C. P.; Bechara, E. J. H. *Trends Mol Med* **2018**, *24* (6), 527–541.

FC 03

Acid catalysed thermal return of diarylethene molecules : a spectroscopic and computational study

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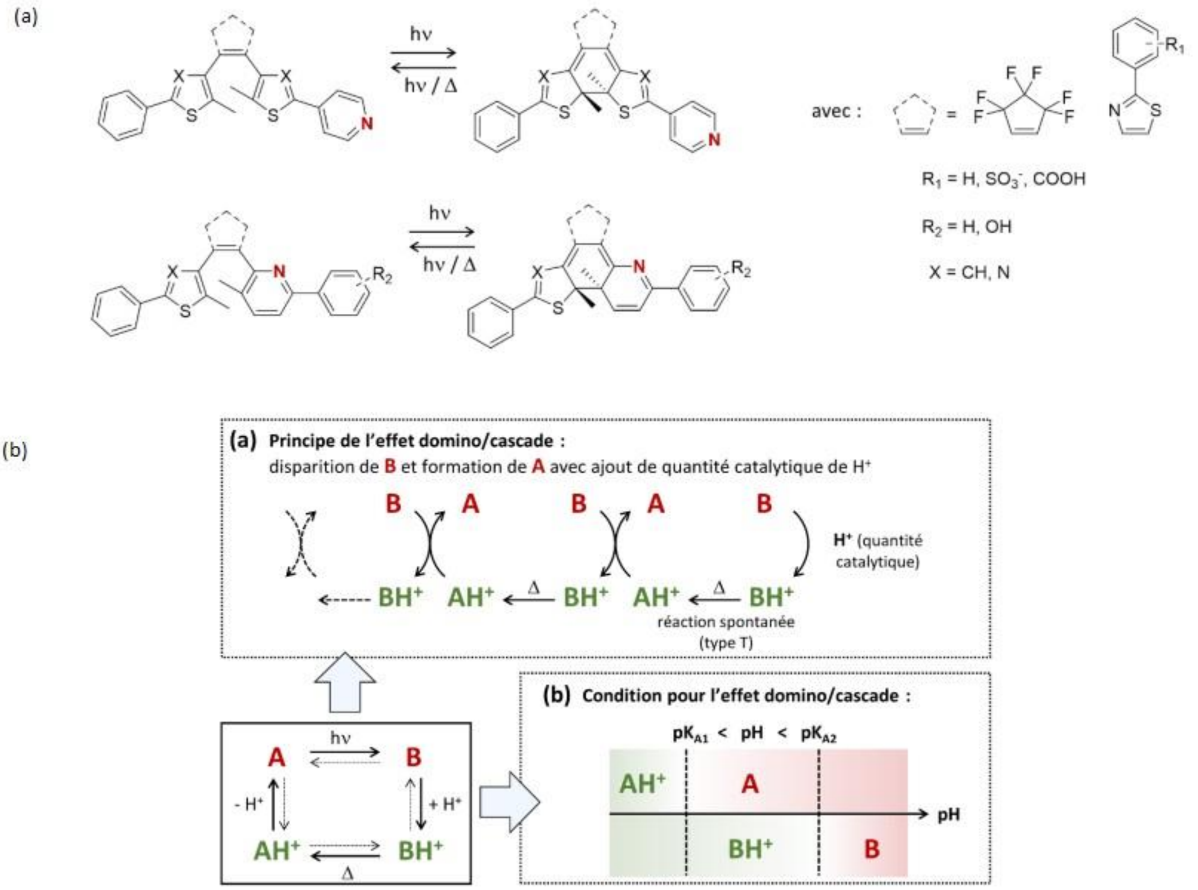
Keywords: Photochemistry, Photochromic molecules, Kinetics, Light energy storage

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. The back reaction can occur either by light irradiation (P type photochrom) or thermally (T type photochrom).

In this context, we studied two diarylethene derivatives with pyridine moiety (Fig 1a) : both molecules exhibit a thermal stability in a neutral environment and a thermal back return in an acidic environment, due to the protonation of the pyridine moieties. Moreover, the thermal back return rate reaction is strongly dependant on the concentration of acid, even at high acid equivalents, suggesting an original mechanism.

Moreover, pKa calculations predict that only a catalytic amount of acid could be used to generate a total recovery of the stable isomer, through a cascade effect (Figure 1b). Thus, this can lead by a catalytic “on demand” thermal back reaction of the photochromic molecule, which opens the possibility to store light energy and convert it on demand to thermal energy with a great control on the system.



(a) General structure of studied molecules. (b) Mechanism of the cascade effect for the spontaneous return B -> A and pKa conditions on the acido-basic couples

FC 04

SYNTHESIS OF BIOBASED MATERIALS WITH ANTIBACTERIAL PROPERTIES

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Keywords: photochemistry, antibacterial, biobased material, visible light, new photosensitizer, reactive oxygen species.

Photochemistry is a material synthesis method close to a "green" chemistry because it allows fast syntheses, without solvents, and requires only low energy consumption [1–2]. In this project, photochemistry was used to produce a new biobased material with antibacterial properties. To synthetize this material, epoxy photoreactive functions were grafted on alizarin, a natural dye derived from madder roots, which was then used as a photosensitizer. The aim was to integrate this alizarin derivative into the polymer network during the cationic photopolymerization. The monomers used were a mixture of two eugenol derivatives (mono- and di- epoxy), a molecule extracted from cloves. This new photosensitizer demonstrated an excellent ability to initiate polymerization under visible light irradiation (LED@405nm). The characterization of the photophysical and photochemical properties of the photoinitiator system have been fully described by spin-trapping EPR, laser flash photolysis and fluorescence.

In this project, photochemistry is used both to synthesize the material and also to induce its antibacterial properties. Indeed, under white light irradiation, the photosensitizer trapped in the polymer network is able to generate reactive oxygen species which are known to be biocide [3]. Experimentally, the materials irradiation allowed a total elimination of *Staphylococcus aureus* and *Escherichia coli* deposited on their surface.

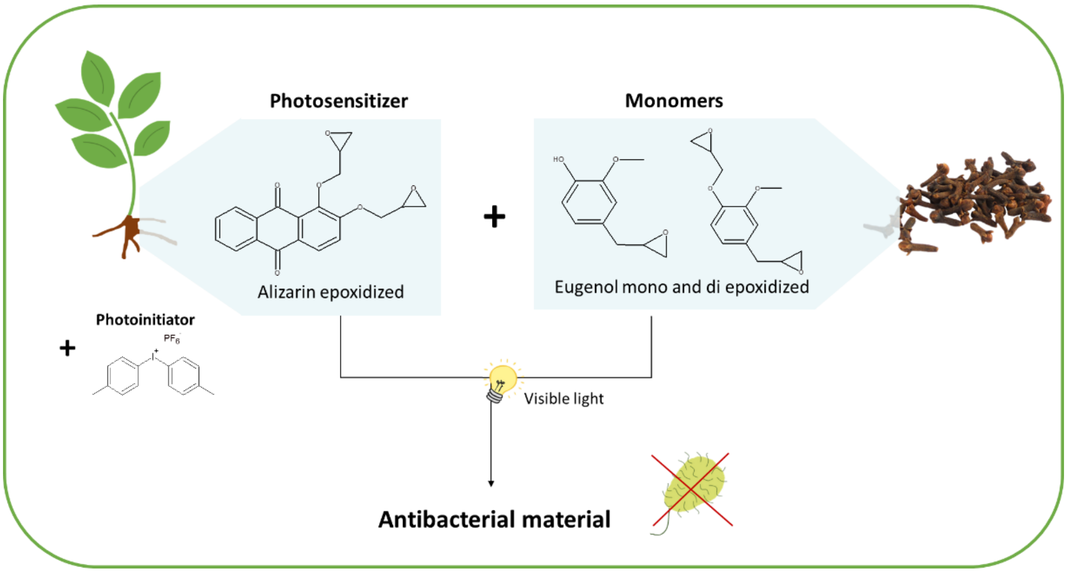

Figure 1: *Synthesis of biobased and antibacterial materials.*

[1] Yagci Y, Jockusch S and Turro N J 2010 Photoinitiated Polymerization: Advances, Challenges, and Opportunities *Macromolecules* **43** 6245–60 [2] Pierau L, Elian C, Akimoto J, Ito Y, Caillol S and Versace D-L 2022 Bio-sourced Monomers and Cationic Photopolymerization: The Green combination towards Eco-Friendly and Non-Toxic Materials *Progress in Polymer Science* 101517
[3] Sautrot-Ba P, Jockusch S, Malval J-P, Brezová V, Rivard M, Abbad-Andaloussi S, Blacha-Grzechnik A and Versace D-L 2020 Quinizarin Derivatives as Photoinitiators for Free-Radical and Cationic Photopolymerizations in the Visible Spectral Range *Macromolecules* **53** 1129–41

FC 05

Sustainable fabrication of fluorescent carbon quantum dots (CQDs)

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Keywords: Carbon Quantum Dots, Life Cycle Assessment, Bottom-up synthesis, Organic waste

Carbon Quantum Dots (CQDs) are fluorescent carbon-based nanomaterials that possess remarkable physicalchemical properties, which allowed them to emerge as an alternative for traditional fluorophores in applications such as bioimaging, drug delivery or in light-emitting devices [1,2]. Namely, these possess characteristics such as biocompatibility, water solubility, low toxicity, strong(er) luminescence, good (photo)chemical stability. Moreover, CQDs can be obtained from a wide number of commercial organic molecules, typically under bottomup procedures (as hydrothermal and microwave-assisted synthesis), as these processes have the advantages of being simple, low cost and potentially suitable for mass production [3]. However, some of the used precursors can be expensive, while their use/production can present challenges to the environment and human health.

Herein, the objective of this work is to develop more environmentally sustainable fabrication strategies for CQDs. The first step was then to evaluate the environmental impacts of typical bottom-up routes, as well as the main responsible for them. To that end we performed a Life Cycle Assessment (LCA), which allows to quantify the potential environmental impacts of a given system during its life cycle [4,5]. This study showed that main hotspots for environmental impacts for this synthesis are the identity of carbon precursor and the amount of consumed electricity [4].

Following on this finding, we next aimed to incorporate organic waste as carbon precursor, to reduce the use of commercial reagents. Different types of organic waste were tested as sole precursor, but the obtained fluorescence quantum yields (QY_{FL}) were too low (~1%). However, when the different types of waste were used to reduce the amount of consumed chemical reagents, to obtain CQDs prepared from mixtures of citric acid and ethylenediamine, QY_{FL} up to ~40% were achieved. Thus, the use of organic waste as part of carbon precursors leads to more environmentally sustainable CQDs with relevant QY_{FL}.

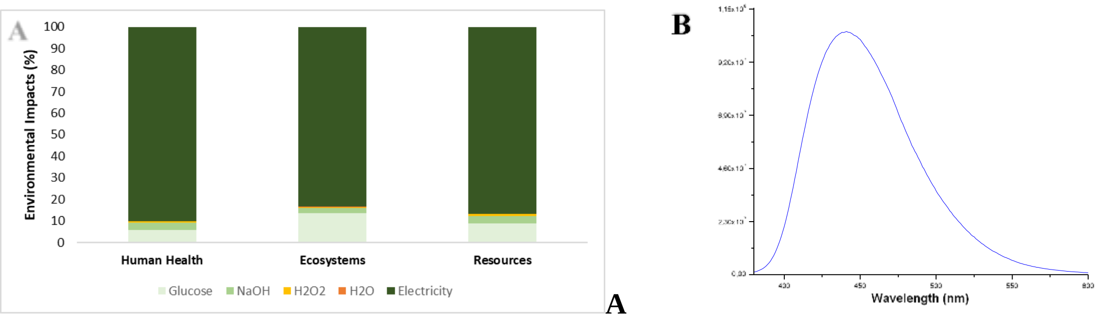

Figure 1. **(A)** Relative environmental impacts of a bottom-up high-yield synthesis, applying ReCiPe method. **(B)** Emission spectrum of CQD with QY_{FL} ~40%.

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References.

[1] Esteves da Silva, J.C.G., Gonçalves, H.M., TrAC Trends Anal. Chem., **2011**, 30, 1327–1336.

[2] Liu, J., Li, R., Yang, B., ACS Cent. Sci., **2020**, 6, 2179−2195.

[3] Crista, D.M.A., Esteves da Silva, J.C.G., Pinto da Silva, L., Nanomaterials, **2020**, 10, 1316. [4] Fernandes, S., Esteves da Silva, J.C.G., Pinto da Silva, L., Materials, **2022**, 15, 3446.

[5] Fernandes, S., Esteves da Silva, J.C.G., Pinto da Silva, L., NanoImpact, **2021**, 23, 100332.

FC 06

2-PHENYLBENZOTHIAZOLE CYCLOPLATINATED(II) COMPLEXES WITH PICOLINATE LIGANDS. POLYMORPHISM AND REVERSIBLE MECHANOCHROMIC BEHAVIOR

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Keywords: Polymorphism, Mechanochromism, Cycloplatinated, Aggregation.

Cyclometalated Pt^{II} complexes have received great interest due to their potential application in fields as organiclight emitting diodes (OLEDs), dye-sensitized solar cells (DSSC), hydrogen production, chemical sensing and bioimaging. The square-planar geometry and the coordination of flat and delocalized ligands favors Pt···Pt and /or □··· □ intermolecular interactions, able to generate extended chains and/or oligomeric nanostructures displaying, in occasions, polymorphs with distinct stacking arrangements in solid state with modification of their optical properties. These interactions are sensitive to external stimuli and some of these complexes display mechanochromic and/or vapochromic behavior [1].

He, we present new luminescent Pt^{II} complexes with 2-phenylbenzothiazole (pbt) as cyclometalated ligand and two different picolinate ligands [Pt(pbt)(R-pic-□*N*,*O*)] (R= H **1**, OH **2**). Both of them present mechanochromic behavior with high-contrast emission changes and complex **2** exhibits polymorphism in solid state due to the presence of the OH substituent, that allows to modulate the packing through donor-acceptor H-bonding interactions with the CH_2Cl_2 solvent molecules. Three pseudopolymorphs of **2** were isolated including yellow (**2-Y**), orangered (**2-R**) and black one (**2-B**) with emission in the range of the visible to the near infrared. Single crystal studies show that **1** and **2-Y** present a columnar stacking with only weak □···□ interactions, whereas the **2-R** polymorph displays aggregated 1D infinite chains with both Pt···Pt and □···□ interactions. To insight in the nature of the optical properties of the different polymorphs, theoretical calculations (DFT/TD-DFT) of different oligomers have been studied, indicating relevant Pt···Pt interactions, particularly in their T_1 states, associated with a metal-metal to ligand charge transfer transition. Additionally, Noncovalent Interaction (NCI) studies have been carried out.

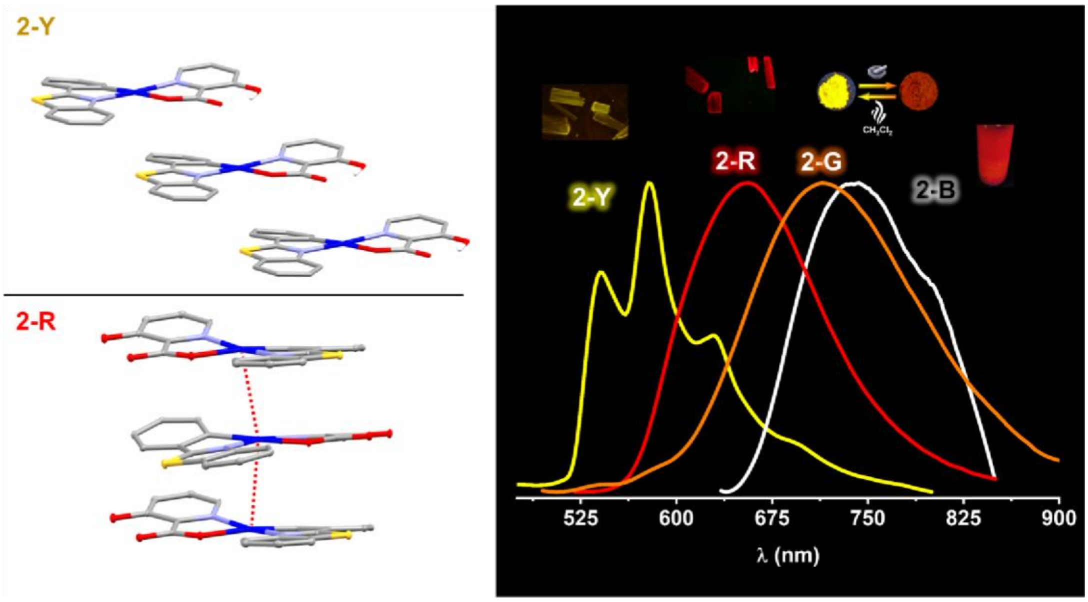

Figure 1. Polymorphism and mechanochromism behavior of complex **2**.

[1] Martínez-Junquera, M., Lalinde, E., Moreno, M. T., Inorganic Chemistry, **2022**, 61, 10898.

FC 07

FUNDAMENTAL INSIGHTS INTO THE CHARGE TRANSFER PATHWAY IN MULTIFUNCTIONAL INORGANIC-ORGANIC HYBRID MATERIALS BY TRANSIENT ABSORPTION SPECTROSCOPY

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Keywords: Transient Absorption Spectroscopy, Artificial Photosynthesis, Charge Transfer Mechanism

Artificial photosynthesis (AP) has emerged as key tool for solar fuels production and CO_2 photoreduction, providing a renewable solution to the global warming. For this purpose, TiO_2 based photocatalysts are widely used owing to its availability at low cost. Unfortunately, TiO_2 is active only under UV light (~4% of solar energy), while visible light contributes ~43%, resulting in a low AP pathways efficiency. In this context, the development of novel photocatalysts absorbing from UV to visible light is still needed. With this idea in mind, we propose the design of new multifunctional hybrid materials based on Organic Polymers (OP, such as Conjugated Porous Polymers) and inorganic semiconductors (ISs, such as TiO_2) as photocatalysts driving more efficiently photoactivated reactions under UV-visible light [1]. Upon light exposure, a charge transfer could occur in these materials to transform CO_2 and H_2O in fuels. As a consequence, understanding the charge separation and transfer events in these hybrids is required for elucidated the mechanism involved in AP photocatalytic processes (Figure 1). Herein, we demonstrate the usefulness of the photophysical techniques by means time-resolved fluorescence and Transient Absorption Spectroscopy (from the femtosecond to second timescale) to establish the mechanism governing the photocatalytic efficiency in hybrids photocatalysts under UV-visible light [2,3]. The unique interfacial interaction between OP and IS results in longer carriers' lifetimes from the ns to s timescale. These findings demonstrate a higher driving force for the electron transfer, which directly lead to an enhanced performance of the hybrids based on OPs and ISs compared to the bare materials. These results establish the key between performance-structure relationships and highlight the great potential of highly tunable OPs for solar fuels production, as well as for a multitude of lightmediated energy applications.

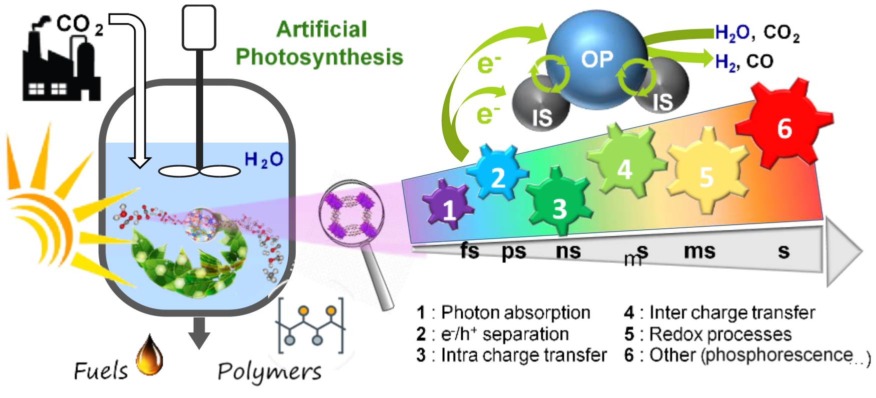

Figure 1. Scheme of the photochemical events involved on artificial photosynthesis process.

Acknowledgements: Financial support was received from the European Union's Horizon 2020 research and innovation program under European Research Council (ERC) through the HyMAP project (grant agreement No. 648319) as well as the Nympha Project (PID2019-106315RB-I00).

[1] M. Barawi, L. Collado, M. Gomez-Mendoza, F. E. Oropeza, M. Liras, V. A. de la Peña O'Shea, Adv. Energy. Mater., **2021**, 11, 2101530.

[2] M. Gomez-Mendoza, M. Pintado-Sierra, C. Monterde, M. Barawi, F. Sánchez, M. Iglesias, V. A. de la Peña O'Shea, M. Liras, Advanced Sustainable Systems, **2022**, 6, 2200160.

[3] L. Collado, M. Gomez-Mendoza, M. García-Tecedor, F. E. Oropeza, A. Reynal, J. R. Durrant, D. P. Serrano, V. A. de la Peña O'Shea, Applied Catalysis B: Environmental., **2023**, 324, 122206.

FC 08

To Link or not to Link?:
Sensitizer-Catalyst Dyads for Photocatalytic CO_2 Reduction

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Keywords: photocatalysis, CO_2 reduction, time-resolved spectroscopy, charge accumulation

Reduction of carbon dioxide (CO_2) into energy-rich compounds using solar light as an energy source provides a sustainable approach to solving the problem of global warming. Natural photosynthesis already provides us with the inspiration to utilize abundant resources of water, CO_2, and sunlight to produce energy-rich products. Mimicking this scheme usually involves synthesizing supramolecular assemblies that contain a *sensitizer* able to harness solar energy and delivering the generated charges to *catalysts* to perform specific reactions. In this strategy, the choice of the bridging ligand plays important roles in conveying efficiently the electrons in a controlled fashion, and helping to maintain a spatial and temporal charge accumulation in the catalyst for eventual use in the multielectron CO_2 reduction. Analysis of the choice of bridging ligands in the literature points to an unexpected contradiction. On one hand, the use of linkers promoting strong electronic communication accelerates electron transfer from the sensitizer to the catalyst but results in lowered photocatalytic activities, while on the other hand, weaker electronic communication provides better photocatalytic activities even with low thermodynamic drive for the first photo-induced electron transfer. This suggests that the rate-limiting step may not be the first electron transfer but the subsequent steps. As most studies focused on the effect of the bridging ligand on the formation of the one-electron reduced species of the catalyst, the photo-induced formation of the catalytically active doublyreduced form has yet to be more profoundly investigated.

In order to address this critical task, we have developed a double-excitation nanosecond pump-pump-probe setup to track sequential charge accumulation at the catalyst. A novel triazole-linked ruthenium sensitizer and a rhenium catalyst dyad was synthesized and investigated for such photo-induced charge accumulation.[1] The triazole bridge promoted weak electronic communication between the two units, resulting in an anodic shift of the reduction potentials of the Re moiety. Upon excitation of the sensitizer, the first reduction of the catalyst occurred with a fast apparent rate of $>5\times10^7$ s. Using a double-excitation setup to track the second electron accumulation on the catalytic unit, however, was not conclusive as no observable absorption changes occurred upon the second excitation. This suggests a pathway for an efficient intramolecular reverse electron transfer preventing the twoelectron accumulation at the catalyst. Nevertheless, under continuous irradiation and with the use of sacrificial electron donors, photocatalytic CO_2 reduction assays showed good turnover numbers, hinting at the non-innocent role of byproducts in the solution.

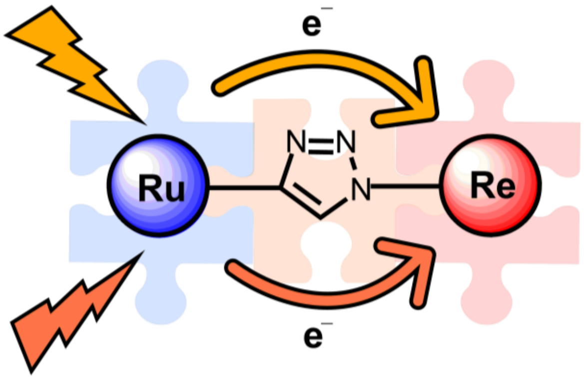

Figure 1. Invesigation of photo-induced two-electron accumulation in a Ru sensitizer – Re catalyst dyad linked by a triazole bridge.

[1] P. Gotico, T.-T. Tran, A. Baron, B. Vauzeilles, C. Lefumeux, M.-H. Ha-Thi, T. Pino, Z. Halime, A. Quaranta, W. Leibl, A. Aukauloo, *ChemPhotoChem* **2021**, *5*, 654–664.

FC 09

A Re(I) PhotoCORM-cellulose nanocrystal scaffold for promising antibacterial phototherapy

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Keywords: Rhenium(I), PhotoCORM, cellulose nanocrystals, antibacterial, carbon monoxide, singlet oxygen.

Since the widespread use of antibiotics, many pathogenic bacteria have developed resistance mechanisms and scientists are focused to find alternative solutions to fight them. For the past decade, carbon monoxide (CO) has been increasingly used for its antiproliferative effect on microbes. However, given the toxicity of CO, it is necessary to use it very carefully. For this reason, photochemically CO-releasing molecules (photoCORMs), which can deliver CO in a timely and spatially controlled way when excited by light, have attract attention [1]. Remarkably, photoCORMs have proved to be much more efficient bactericides than CO gas alone, possibly due to the synergistic effect of CO and the generation of reactive oxygen species (ROS), concomitantly produced by the photoreaction.

Original photoCORMs based on stable and biocompatible tricarbonyl-rhenium(I) complexes have been recently developed in our team [2]. The fast photoproduction of CO (within minutes) is accompanied by the slow but continuous production of singlet oxygen ($^1O_2$) over hours. In addition, phosphorescence variations allow easy monitoring of the photoreaction. However, improving the water solubility of our photoCORMs as well as their specificity towards dangerous bacteria is required. Therefore, cellulose nanocrystals (CNCs), a well-known biocompatible and sustainable material, was used as a platform, with the aim to gather both photoCORMs and some targeting agents in a non-covalent, highly versatile way [3]. In this communication, the association of PhotoCORMs with CNCs will be discussed. Preliminary tests show that this system offers promising perspectives for fighting antibioresistant bacteria.

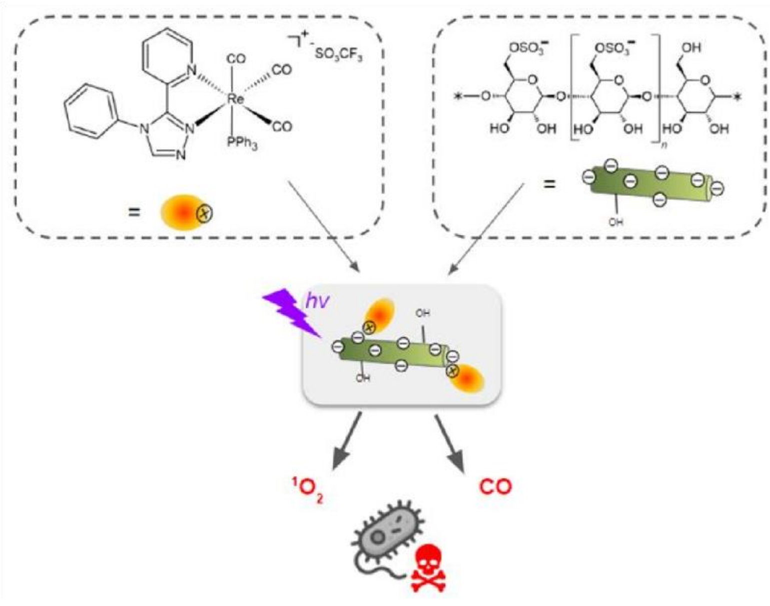

Figure 1. A photoactive Re(I) photoCORM-CNCs system against bacteria.

[1] E. Kottelat, F. Zobi. Inorganics. **2017**, 5, 24.

[2] Á.D. Hernández Mejías, A. Poirot, M. Rmili, N. Leygue, M. Wolff, N. Saffon-Merceron, E. Benoist, S. Fery-Forgues. Dalton Trans. **2021** , 50: 1313– 1323.

[3] G. M. A. Ndong Ntoutoume, R. Granet, J.-P. Mbakidi, E. Constantin, L. Bretin, D. Y. Léger, B. Liagre, V. Chaleix, F. Brégier, V. Sol. Med. Chem. Lett. **2021**, 41, 128024.

FC 10

Comparative study of morphological and optical properties of Synthesized Platinum-Bismuth alloy powders

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Keywords: Bismuth-Platinum powder, Chemical synthesis, Optical properties.

Abstract- In this comparative study, the powdered bismuth-platinum alloy (BiPt-PW) was synthesized by a chemical method, using $NaBH_4$ as reducing agent, polyvinylpyrrolidone (PVP) and gum arabic (GA) as capping agents. Guan et al. [1], studied the FePt@PtBi intermetallic core-shell. Nan et al. [2], prepared platinum-bismuth supported on silica. The BiPt-PWs synthesized in this work were characterized by several techniques. The XRD characterization confirms the formation of the crystalline phase of the BiPt alloy for the first powder, for the 2nd and 3rd in the presence of GA and PVP, respectively, the composition of the powders has been changed. The UV-Vis spectrum for the BiPt-PWs corresponds to the Pt^{+4} and Bi^{+3} ions (in solution) and for the solid UV-Vis, figure 1., the absorption of the synthesized PWs, changes according to the protective agent used, compared with the powder synthesized without the presence of these molecules, this variation is due to the change in particle sizes, which is directly related to the surface plasmon resonance.

REFERENCES

1. Guan, J., Yang, S., Liu, T., Yu, Y., Niu, J., Zhang, Z., & Wang, F., *Intermetallic FePt@ PtBi core–shell nanoparticles for oxygen reduction electrocatalysis*, ***Angewandte Chemie, 133.40,*** (22070-22075) (2021), https://doi.org/10.1002/ange.202107437.

Yonggang Feng, Qi Shao, Fan Lv, Lingzheng Bu, Jun Guo, Shaojun Guo, Xiaoqing Huang, *Intermetallic PtBi nanoplates boost oxygen reduction catalysis with superior tolerance over chemical fuels*, ***Advanced Scienceature, 7.1,*** (1800178) (2021), https://doi.org/10.1002/advs.201800178.

FC 11

THE ROLE OF CYTOCHROME C-CARDIOLIPIN COMPLEX IN LIPID PEROXIDATION AND APOPTOSIS: KINETIC CONSTANTS AND QUANTUM YIELDS, CALCULATED FROM ACTIVATED CHEMILUMINESCENCE KINETICS.

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Key words: Cytochrome c, peroxidases, nanomachine , peroxidases, mathematical modeling, quantum yield

Cytochrome C in combination with membrane cardiolipin, acquires peroxidase activity, catalyzes lipid peroxidation and triggers apoptosis along the mitochondrial pathway. The use of its natural apoptogenic properties can be an effective method in the chemotherapy of oncological diseases. To develop this direction, a detailed study of its apoptogenic activity is necessary, requiring the most accurate selection of the kinetic parameters of the system. In this paper, an algorithm for calculating these parameters based on the kinetics of activated chemiluminescence with visualization of the obtained model curves and their comparison with experimental data is developed. Obtaining accurate kinetic parameters of the system allows us to evaluate the structure of the cytochrome C complex with cardiolepin. which is a nanoglobule of partially melted protein with fatty acid residues of cardiolepin penetrating into it.

As part of the study of the properties of various substances suitable for chemotherapy of oncological diseases, a natural apoptogen was studied – a cytochrome c complex with cardiolipin, which is a catalyst for the process of lipid peroxidation and a trigger of apoptosis [1]. The processes of peroxidation were monitored by the kinetics of activated chemiluminescence (CL) [Vladimirov Yu.A.], using a specially developed software product that allows optimizing the modeling of processes occurring in the system and calculating the kinetic parameters of the system as accurately as possible. In the course of the work, changes in the intensity of CL were modeled in different spectral regions, depending on the concentration of the activator [1].

Coumarin dye C-525 was used as a physical activator of CL lipids (which does not affect the basic processes occurring in the system and does not change the kinetics of CL), increasing its intensity by 3 orders of magnitude due to triplet-triplet energy transfer from excited levels of carbonyls L=O* formed in the reaction of disproportionation of lipoperoxyl radicals LOO*, which, in turn, are generated by lipid peroxidation. Software was developed to calculate the quantum yield of CL in the presence of coumarin C-525; the nature of the luminescent process was controlled by the CL spectrum, which differs between the activated and its own CL system.

In the course of solving the problem, optimization was proposed: several algorithms for solving this problem in C++ were considered and implemented, each of which was compared step by step with an experiment. An effective solution was found by the least squares method.

Parameters were selected for modeling kinetic curves of luminescence attenuation in the form:

$$I_{\text{люм}} = 2{,}303 \varepsilon l c \eta k I_{\$} \quad .$$

The quantum yield of chemiluminescence is calculated and modeled: $\eta_{cL}=\eta_T*\eta_{ph}$.

It has been shown that cardiolipin plays the role of a proton trap, stabilizing the pH in the intermembrane space [1,2].

An analysis method has been developed for the diagnosis of diseases associated with pathological cell apoptosis in the form of an algorithm for automatic calculation of kinetic parameters of lipid peroxidation by the kinetics of activated chemiluminescence and visualization of the obtained model curves and selection of reagents.

We would like to express our gratitude to the leaders for their valuable contribution to the planning of the study, Academician Professor Yuri Andreevich Vladimirovu, Faculty of Fundamental Medicine of Moscow State University and Professor Anatoly Nikolaevich Osipov, Faculty of Biomedical Sciences of the Russian National Research Medical University named after N.I. Pirogov

References

[1] . Vladimirov Yu.A., Vladimirov G.K.. Structure and peroxidase function of the cytochrome c complex with cardiolipin in an aqueous medium and in a non-polar environment. 2018

[2] . Haines T. H., Dencher N. A. Cardiolipin: a proton trap for oxidative phosphorylation // FEBS letters. – 2002. – V. 528. – № 1-3. – P. 35-9.

FC 12

ON THE DETERMINATION OF THE ABSORTION CROSS SECTIONS OF ClOOCl BY MULTICONFIGURATIONAL QUANTUM CHEMISTRY AND PROBABILISTIC MACHINE LEARNING

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Keywords: ClOOCl, CASPT2, GMM-NEA

In 1985, the scientific community detected a substantial reduction in the thickness of the ozone layer over Antarctica that could not be explained by the catalytic cycles known at the time to destroy ozone. After several research studies, it was possible to establish the chemical mechanism responsible for this phenomenon, in which one of the species proposed as relevant is the ClOOCl molecule. According to these works, its absorption of sunlight gives rise to the Cl atom, which reacts efficiently with O_3. Despite the great advances in this field, there is still some debate regarding the exact contribution of this species, because there are uncertainties in the amount of sunlight it absorbs in the spectrum where there is more actinic solar flux in the stratosphere (>300 nm) and in the determination of the photochemical generation rates of Cl. [1]

The goal of the present study is to theoretically determine the sunlight absorption intensities of the ClOOCl molecule, analyze different factors that can affect such determinations and compare the generated spectrum with other computed and experimental spectra reported in the literature. [1,3] For that, we are following a 3-steps approach: firstly, a representative set of quantum geometries are obtained by the Nuclear Ensemble Approach (NEA) reproducing a Wigner distribution, secondly, multiconfigurational quantum chemistry (the CASPT2 method) is used to compute the vertical excitation energies (ΔE) and oscillator strengths (f) for several electronic states at each geometry of the ensemble, and thirdly the Gaussian Mixture Model NEA (GMM-NEA) method [2] is employed to reconstruct the spectrum based on the data of the second step. Among the theoretical factors affecting the spectrum, we have considered the basis set, the frequencies used to generate the Wigner geometries, the spinorbit coupling or the number of excited states.

[1] NASA JPL Publication 19-5, 2019

[2] Luis Cerdán, Daniel Roca-Sanjuán, J. Chem. Theory Comput. 2022, 18, 3052−3064

[3] Milan Ončák, Lukáš Šištík and Petr Slavíček, J. Chem. Phys. 133, 174303 (2010)

FC 13

Design and synthesis of UV filters based on natural products

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Keywords: UV filters, photoprotection

Solar radiation is responsible for several important photochemical and photobiological reactions that may lead to cancer or death depending on different factors as the duration of exposure.[1]

UV radiation (100-400 nm) is classified into UVA, UVB and UVC but only UVA and UVB are responsible for causing damage to the skin because UVC is blocked by the ozone layer. So, in this context, to minimize this problem is necessary to develop new compounds with adequate photoprotecting mechanisms suitable for human use. Ideally, these new UV filters should feature certain characteristics such as high stability, an efficient energy dissipation mechanism, strong UV absorption and biodegradability.[2]

In this work, we have synthesized a great variety of UV filters that present their absorption band in the UV-Vis range and to design these compounds, we have focused our attention on the structure of natural photoprotective molecules because they have an appropriate mechanism of photoprotection. After the design and synthesis stages, we explored the ability to photoprotect different surfaces as the human skin based on the analysis of the photoprotection mechanisms by computational methods, the measurement of the absorption band (shape and position) and the study of stability to select the compounds with the best photoprotection characteristics.

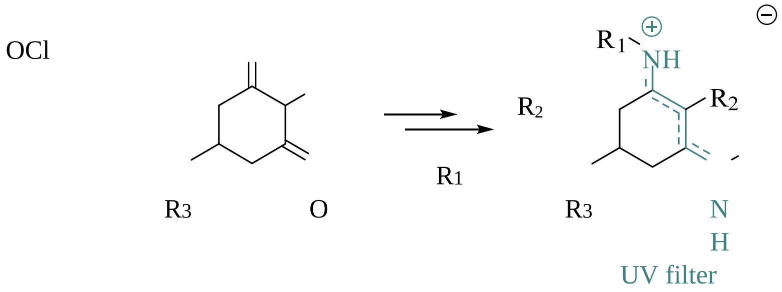

Figure 1. Scheme of synthesis of UV filters.

[1] Guan, L. L.; Lim, H. W.; Mohammad, T. F. Am. J. Clin. Dermatol. 2021, 22 (6), 819–828.

[2] Losantos, R.; Funes-Ardoiz, I.; Aguilera, J.; Herrera-Ceballos, E.; García-Iriepa, C.; Campos, P. J.; Sampedro, D. Angew. Chem. Int. Ed. 2017, 56 (10), 2632–2635.

FC 14

Phenothiazine and carbazole based stable hole-transporting materials for Emerging Hybrid Photovoltaics

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Keywords: Perovskite based solar cells, Holes Transporting materials (HTMs), small molecule HTMs, polymer HTMs

Perovskite based Solar Cells (PSCs) experienced a fast progress in the research, suggesting their great potential. Indeed, in few years an impressive efficiency of 25.5% has been reached, that has been further increased to 30% with Perovskite/Si tandem device architectures.[1] Good device performances are achieved with the presence of an Electron Transporting Material (ETM) and a Hole Transporting Material (HTM) surrounding the photoactive Perovskite layer: they drain efficiently the light-generated charges towards the corresponding electrodes.

However, the industrial production of PSCs is still hampered by their low long-term stability.[2] In particular, the salts used for doping of HTMs are highly hygroscopic, thus favouring the degradation of the Perovskite layer. In this context, the project of the research is focused on finding new "low dopant" or "dopant-free" conductive HTMs [3], possessing passivation properties toward the photoactive layer to reduce the degradation induced by both light and extrinsic factors. Starting from phenothiazine and carbazole scaffolds, low-cost materials with favourable and easily tuneable electronical properties, small molecule and polymer HTMs will be synthesized. In the present work, the 3,3'-(9-hexyl-9H-carbazole-3,6-diyl)bis(10-hexyl-10H-phenothiazine) (A) and 10-hexyl-3,7bis(9-hexyl-9H-carbazol-3-yl)-10H-phenothiazine (B) were synthesized and structurally, optoelectronically and electrochemically characterized. Both molecules demonstrated to have HOMO values well suited for their application in PSCs.

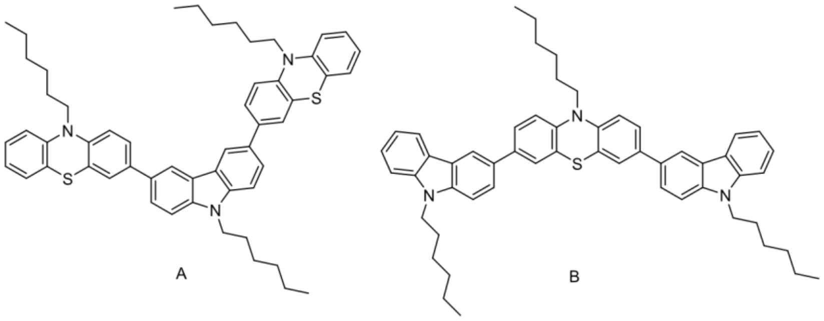

Figure 1. Small molecules HTMs.

[1] https://www.nrel.gov/pv/cell-efficiency.html.

[2] C. C. Boyd, R. Cheacharoen, *Chem Rev*, **2019,** 119, 3418-3451.

[3] M. M, H. Desoky, M. Bonomo, *Energies*, **2021,** 14, 2279 - 2328.

FC 15

RED THERMALLY-ACTIVATED DELAYED FLUORESCENCE IN PHENOTHIAZINE-NAPHTHALIMIDE DERIVATIVES

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Keywords: Delayed fluorescence, intersystem crossing, reverse intersystem crossing, intramolecular charge transfer, time-resolved spectroscopy

A series of new purely organic phenothiazine-naphthalimide derivatives has been studied to investigate Thermally-Activated Delayed Fluorescence (TADF) for applications in optoelectronics. The systems showed a relevant structural effect. The oxygen-free molecules exhibited red emission with lower quantum yield with respect to the oxidized ones. In addition, the series with a phenyl group as linker between the donor-acceptor moieties were characterized by greater fluorescence quantum yields compared to the C-C bridged molecules, which, contrary, showed a more efficient intramolecular charge transfer (ICT) behaviour. Nanosecond and femtosecond time-resolved spectroscopies of the compounds in solvents with increasing polarity have been employed to study the triplet state population and the excited states dynamics. Experiments at low temperature (77K) were performed to detect the phosphorescence emission of the compounds. The evidences suggest a significative production of ICT states, even in solvents with low polarity. The oxygen-free phenothiazine-naphthalimide derivatives shows efficient intersystem crossing (ISC) and a small energy gap between the singlet and the triplet excited states. These systems exhibited long fluorescence lifetimes, in the order of hundreds of nanoseconds, that increased to orders of thousands of nanoseconds in the nitrogen purged solutions. For the oxidized compounds and for the phenyl-bridged systems the singlet excited states are too high with respect to the triplet states. Therefore, even if the ISC process is efficient, the reverse intersystem crossing (rISC) can not occur. The experimental results are consistent with theoretical calculations conducted to predict the nature of the transitions and the molecular orbitals. The red TADF with long lifetimes detected only in the oxygen-free compounds demonstrates that the distance between the donor and the acceptor units and their spatial separation is fundamental to promote the rISC which leads to the delayed fluorescence.

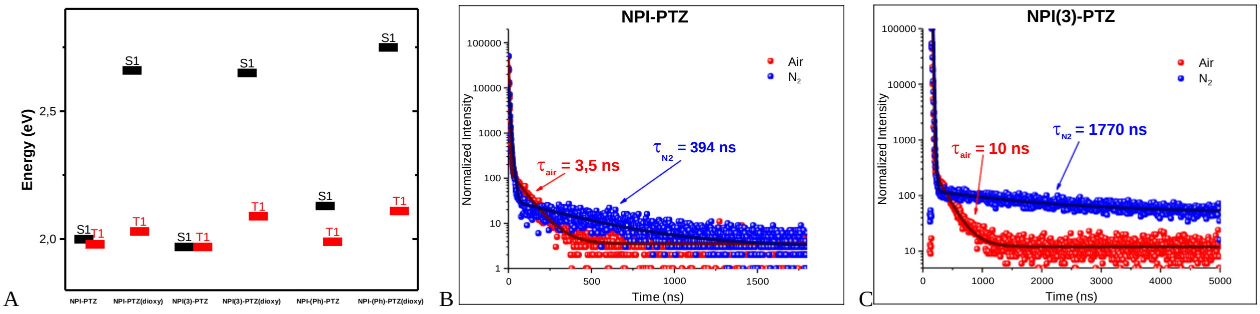

Figure 1. (A)Energy levels of the singlet and triplet excited states of the investigated compounds. (B) Fluorescence decay curve of NPI-PTZ in aerated and nitrogen purged toluene. (C) Fluorescence decay curve of NPI(3)-PTZ in aerated and nitrogen purged toluene.

[1] 'Tuning the Fluorescence and the Intramolecular Charge Transfer of Phenothiazine Dipolar and Quadrupolar Derivatives by Oxygen Functionalization', Y. Rout, C. Montanari, E. Pasciucco, R. Misra* and B. Carlotti*, J. Am. Chem. Soc., **2021**, 143, 9933−9943.

[2] 'Red Thermally-Activated Delayed Fluorescence in phenothiazine-naphthalimide derivatives', C. Montanari, T. Bianconi, G. Cavalletti, M. Sheokand, R. Misra and B. Carlotti, (manuscript in preparation).

[3] 'Red Thermally Activated Delayed Fluorescence and the Intersystem Crossing Mechanisms in Compact Naphthalimide–Phenothiazine Electron Donor/Acceptor Dyads', G. Tang, A. A. Sukhanov, J. Zhao, W. Yang, Z. Wang, Q. Liu, V. K. Voronkova, M. Di Donato, D. Escudero, D. Jacquemin, J. Phys. Chem. C, **2019,** 123, 30171–30186.

[4] 'Highly efficient organic light-emitting diodes from delayed fluorescence', H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, Nature, **2012**, 492, 234–238.

FC 16

FROM LIPID PEROXIDATION TO DNA DAMAGES: STUDY OF THE PHOTOREACTIVITY OF ETHENO ADDUCTS

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Keywords: lipid peroxidation, etheno adducts, dna damage, cyclobutane pyrimidine dimer

Lipid peroxidation is a biochemical process that involves the oxidation of polyunsaturated fatty acids, the components of cell membranes. In this process, highly reactive species, such as α,β-unsaturated aldehydes, are generated and react with DNA bases, forming the so-called **etheno adducts**. These DNA lesions exhibit **mutagenic properties**[1]. Indeed, the increase of lipid peroxidation in inflammatory processes[2] has been related to the high levels of etheno adducts in diseases that can lead to cancer, such as Chron's disease or ulcerative colitis[1]. Consequently, they are excellent **bio-markers** for different types of cancer (lung, colon or prostate cancer). Although heir mutagenic properties have been clearly established, their photoreactivity has not been studied yet.

Here, the attention is centered on the cytosine etheno derivative (eC). Recently, the increase of its singlet excited state lifetime compared to that of cytosine was reported[3], which points toward a **potentially increased reactivity**. A model compound containing two eC covalently linked by a trimethylene bridge was synthesized and irradiated to evaluate its photoreactivity under **direct irradiation** or through a **photosensitization** process. Especially, cyclobutane pyrimidine dimer formation, the most common lesion caused by UV light in DNA, was considered taking into account the possibility of a **[2+2] photocycloaddition** involving the double bond at 5,6 of the cytosine moiety or that of the etheno ring.

The aim of this study is to evaluate how these etheno adducts act in DNA. Their formation already means a damage by itself, but if they can form a CPD-type photoproduct it will cause them to be doubly mutagenic.

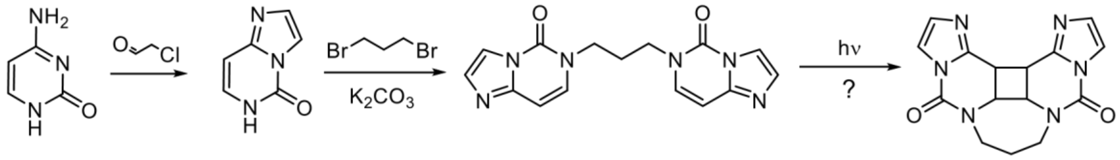

Figure 1. Synthesis and potential photoreactivity of the eC model

[1] U. Nair, H. Bartsch, J. Nair. *Free Radic Biol Med*. **2007**, 43(8), 1109-1120.

[2] A. Winczura; D. Zdżalik; B. Tudek. *Free Radical Res.* **2012**, 46(4), 442–459

[3] P. Lizondo-Aranda , L. Martínez-Fernández , M.A. Miranda , R. Improta, T. Gustavsson, V. Lhiaubet-Vallet. *J. Phys. Chem. Lett.* **2022,** 13, 1, 251–257

FC 17

SOLAR ENERGY STORAGE IN GREEN SOLVENTS

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Keywords: MOST; solar energy storage; solar fuels; norbornadiene; water soluble;

Energy generation and storage has become one of the major challenges in our society. The current energy demand is continuously rising [1] each year by 1.3%. To avoid the environmental impact from conventional energy sources, the use of renewable electricity needs to augment considerably. Using natural photosynthesis as a working model for solar energy use, scientists are designing and preparing chemical systems capable of capturing and storing solar energy. Nowadays, different alternatives to make use of sunlight are under research. In this way, MOST (molecular solar thermal) technology has become a promising candidate to capture and store solar energy in a sustainable and efficient manner.

This research is based on norbornadiene derivatives that is one of the three types of systems that have been mainly used within the current framework of MOST technology (azobenzene and dihydroazulene derivatives are the others) [2].

Until now, all the previous studies are made in carbon-based solvents such as toluene with good results. However, the use of these solvents, that are dangerous for health, is undesired. Along these lines, the main goal of this project is to obtain some norbornadiene derivatives with potential use as MOST systems and with a reasonable degree of solubility in greener solvents.

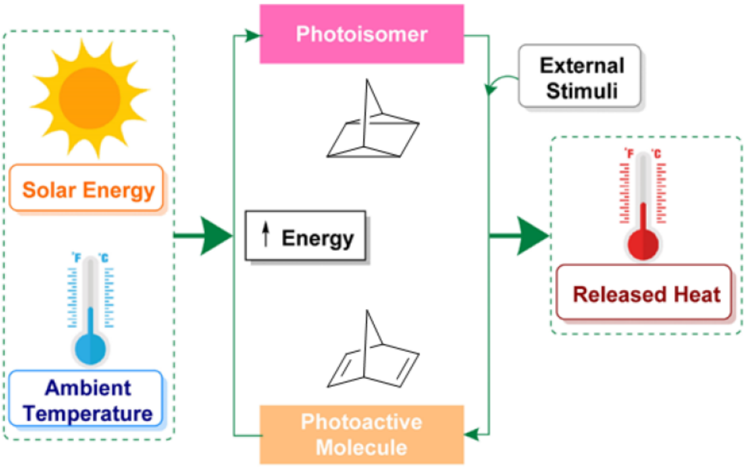

Figure 1. Concept of the MOST system.[2]

[1] Z. Wang; P. Erhart; T. Li; Z.-Y. Zhang; D. Sampedro; Z. Hu; H.A. Wegner; O. Brummel; J. Libuda; M.B. Nielsen; et al., Joule **2021**, 5, 3116–3136.
[2] A. Gimenez-Gomez; L. Magson; B. Peñin; N. Sanosa; J. Soilán; R. Losantos; D. Sampedro, Photochem **2022**, 2, 694–716.

FC 18

Photochemistry of Common Xanthene Fluorescent Dyes as Visible Light Activatable CO–Releasing Molecules

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Keywords: xanthene, fluorescent dye, dye, fluorescein, eosin, rose Bengal, photochemistry, photolysis, carbon monoxide, CORM, photoCORM, photoproducts

Xanthene derivatives are organic dyes, some of which are routinely used in different chemical and biological applications, including human medicine.[1] We investigated the photochemistry of some of the most common ones, fluorescein,[2] eosin Y, and rose bengal,[3] 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 in 40–80% chemical yields upon extensive irradiation with visible light in aqueous solutions during their multistep concomitant degradation processes. In addition, a number of low-mass secondary photoproducts, such as phthalic and formic acids, were identified in the irradiated mixtures.[4] We demonstrate that they can be considered as visible-light activatable CO-releasing molecules (photoCORMs)[5] under specific conditions with potential biological implications and evaluated on a model cell line.[6]

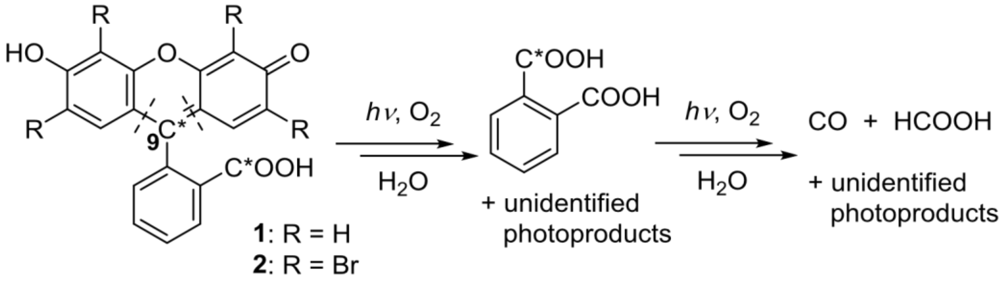

Figure 1. Multiple step multiple-photon excitation visible-light induced photochemical degradation of fluorescein, eosin and rose bengal dyes.

This work was supported by the Czech Science Foundation (GJ20-30004Y), CETOCOEN EXCELLENCE Teaming 2 (CZ.02.1.01/0.0/0.0/17_043/0009632), and RECETOX RI (LM2018121).

[1] WHO, World Health Organization model list of essential medicines: 21st list 2019, 21st edn, **2019**. [2] A. Baeyer, Ber. Dtsch. Chem. Ges., **1871**, 4 (2), 555-558.

[3] L. Ludvíková, P. Friš, D. Heger, P. Šebej, J. Wirz and P. Klán, Phys. Chem. Chem. Phys., **2016**, 18, 16266–16273.

[4] M. Martínek, L. Ludvíková, M. Šranková, R Navrátil, L. Muchová, J. Huzlík, L. Vítek, P. Klán, P. Šebej, Org. Biomol. Chem., **2022**, DOI: 10.1039/d2ob01823c.

[5] P. Šebej and T. Slanina, Photochem. Photobiol. Sci., **2018**, 17, 692–710.

[6] M. Šranková, A. Dvořák, M. Martínek, P. Šebej, P. Klán, L. Vítek and L. Muchová, Int. J. Mol. Sci., **2022**, 23, 1504.

FC 19

INSIGHT INTO THE INTERACTION BETWEEN FLUORESCENT CARBON DOTS AND MOLECULAR BY-PRODUCTS OF THEIR SYNTHESIS

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Keywords: carbon dots; photoluminescence; fluorescent by-products; synergy

Carbon dots (CDs) are carbon-based nanoparticles that present several interesting properties, such as high photoluminescence, broadband absorption, low toxicity, biocompability and good water solubility. CDs can be fabricated using either top-down or bottom-up methodologies, with the most used methods being hydrothermal treatment or microwave-assisted synthesis, both of which are low cost, easy to employ and may lead to relatively different outcomes and environmental impacts [1]. Their unique set of properties and their easy synthesis enables the use of CDs for several applications, including sensing, light emitting devices, photodynamic therapy, photocatalysis, among others [2,3].

Despite all the literature regarding CDs, the origin of their superior photoluminescence is still a highly debated topic. Several explanations have been thus far proposed, including quantum confinement effects, self-trapped excitons, edge states, delocalized surface states and exciton-hole recombination. More recent reports also suggest that a major part of the photoluminescence of CDs prepared via bottom-up routes can be attributed to highly photoluminescent molecular by-products that form alongside CDs during their synthesis [4].

In this work we studied the effects exerted by these fluorescent by-products on the optical and photochemical properties of CDs [5]. Towards this, a citric acid and urea-based CD was produced via a microwave-assisted synthesis and purified via dialysis. This yielded two fluorescent fractions one containing the CD, and the other containing the photoluminescent by-products [5]. Characterization of the fractions via XPS, MS and FT-IR analysis the presence of by-products such as 4-hydroxy-1*H*-pyrrolo[3,4-*c*]pyridine-1,3,6(2*H*,5*H*)-trione (HPPT) (Figure 1) [5]. Furthermore, the photochemical response of both the CD and by-products towards neutral and ionic species revealed an interesting phenomenon. Whereas the by-products do not display any response to those species whatsoever, they effectively increase the photochemical response of the CD towards them [5]. This suggests a synergistic effect between the CD and the by-products resulting from its synthesis, a characteristic that can be exploited to further develop applications for CDs.

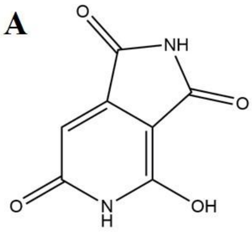

Figure 1. Chemical structure of HPPT.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for funding: PTDC/QUIQFI/2870/2020, UIDB/00081/2020, UIDB/05748/2020, CEECINST/00069/2021and 2021.06149.BD.

[1] Sendão et al., J. Clean. Prod., **2020**, 254, 120080

[2] Sendão et al., Chemosphere, **2022**, 301 (8) 134731

[3] Crista et al., J. Fluoresc., **2019**, 29, 265-270

[4] Kasprzyk et al.. Nanoscale **2018**, 10, 13889

[5] Sendão et al., Phys. Chem. Chem. Phys., **2019**, 21, 20919-20926

FC 20

8-HYDROXYQUINOLINE-2-CARBALDEHYDE AS A TRIBUTYLTIN CHEMOSENSOR

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Keywords: Tributyltin, biocide, chemosensor, quinoline, spectrophotometric titration

Biofouling is a major problem that affects aquatic structures, namely ships, boats, and submerged buildings. Antifouling coatings, with tributyltin (TBT) being one of the most used biocides in their composition, are used worldwide to mitigate this drawback. However, this compound was found to leach from the coatings used in the aquatic structures and to be toxic to aquatic living beings [1–3]. Due to its toxicity, TBT was banned by the Rotterdam Convention. Nevertheless, some countries have not signed this convention, and its effects are still being reported. The available TBT monitoring methods are based on sampling and laboratory analysis; therefore a simple *in-situ* detection method would be of great importance [4].

This work reports the chemosensory studies of 8-hydroxyquinoline-2-carbaldehyde **1** as a TBT optical chemosensor. Preliminary sensory tests were performed with the addition of 50 equivalents of TBT to a solution of **1** in acetonitrile, showing a change of color, from colorless to yellow, with TBT addition. A spectrophotometric titration was performed to assess the number of equivalents required for full interaction and the limit of detection. The results obtained showed that 8-hydroxyquinoline-2-carbaldehyde has promising prospects to be used in the design of more sensitive TBT chemosensors and to be applied on more advanced devices for TBT detection in real time on aquatic environments.

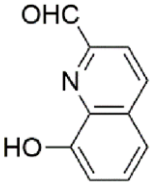

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Figure 1. Structure of 8-hydroxyquinoline-2-carbaldehyde **1**.

References:
[1] Antizar-Ladislao, B. *Environ. Int.* **2008**, *34* (2), 292–308.
[2] Laranjeiro, F.; Sánchez-Marín, P.; Oliveira, I. B.; Galante-Oliveira, S.; Barroso, C. *Environ. Pollut.* **2018**, *232*, 411–421.
[3] Tornero, V.; Hanke, G. *Mar. Pollut. Bull.* **2016**, *112* (1–2), 17–38.
[4] Sousa, R. P. C. L.; Figueira, R. B.; Costa, S. P. G.; Raposo, M. M. M. *ACS Sens.* **2020**, *5* (12), 3678–3709.

FC 21

NEAR-INFRARED POLYMETHINE DYES FOR FLUORESCENCE IMMUNOASSAYS

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Keywords: heptamethine dyes, cyanines, click reaction, CuAAC reaction, bioconjugation, fluorescence.

Small-molecule fluorescent probes and their bioconjugates have become powerful tools to for example advance the field of cell biology, discover new drugs, detect environmental contaminants, and identify cancer. Coumarins, naphthalimides, fluorescein and its analogues, rhodamine, BODIPYs, cyanines and squaraines are examples of fluorophore scaffolds that have been successfully used in the preparation of fluorescent probes.[1]

Cyanines belong to a family of polymethine dyes. Typical cyanine dyes are characterized by two nitrogencontaining heterocycles as end-groups connected with a polymethine chain comprising an odd number of carbon atoms.
Heptamethine cyanine dyes (Cy-7) emits at around 800 nm.[2]

There is a strong demand for such dyes emitting in the red part of the visible spectrum and in the near-infrared, especially in the tissue transparent window (650–950 nm) – where tissues absorption is minimal.[3] Only one such dye approved for use in human medicine – indocyanine green – is known at the moment.

We prepared a small library of cyanines with a linker attached on the heptamethine fluorophore using a newly established synthetic route based on a condensation between a pyridinium salt (Zincke salt) with suitable end-groups (Figure 1).[4] The terminal aryls are substituted with different functional groups to address their electronic and steric effects on the dye's properties.

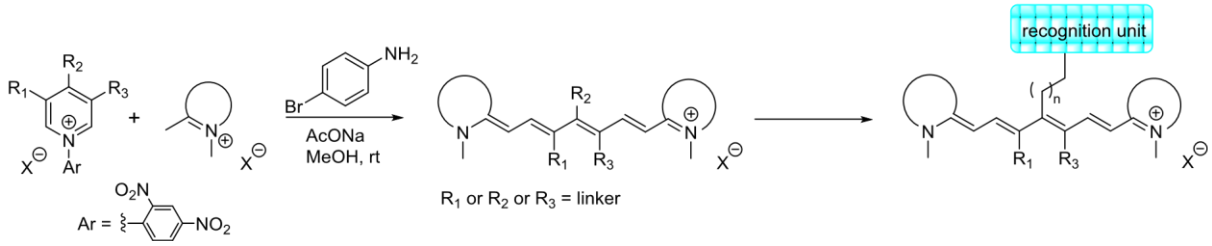

Figure 1. Synthesis of cyanines with linker attached to the heptamethine chain of the fluorophore.

The properties of the dyes in the library (with emphasis on the photophysical properties) were studied and further, the Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC)[5] was used to conjugate the cyanine dyes with antibodies and evaluate the fluorescence emission properties of the bioconjugates.

This work was supported by the Czech Science Foundation (GJ20-30004Y), CETOCOEN EXCELLENCE Teaming 2 (CZ.02.1.01/0.0/0.0/17_043/0009632), and RECETOX RI (LM2018121).

[1] Fu, Y.; Finney, N. S. *RSC Adv.* **2018**, *8* (51), 29051–29061.
[2] Štacková, L.; Muchová, E.; Russo, M.; Slavíček, P.; Štacko, P.; Klán, P. *J. Org. Chem.* **2020**, *85* (15), 9776–9790.
[3] Weissleder, R. A *Nat. Biotechnol.* **2001**, *19*, 316–317.
[4] Štacková, L.; Štacko, P.; Klán, P. *J. Am. Chem. Soc.* **2019**, *141* (17), 7155–7162
[5] Pickens, C. J.; Johnson, S. N.; Pressnall, M. M.; Leon, M. A.; Berkland, C. J. *Bioconjugate Chem.* **2018**, *29* (3), 686–701.

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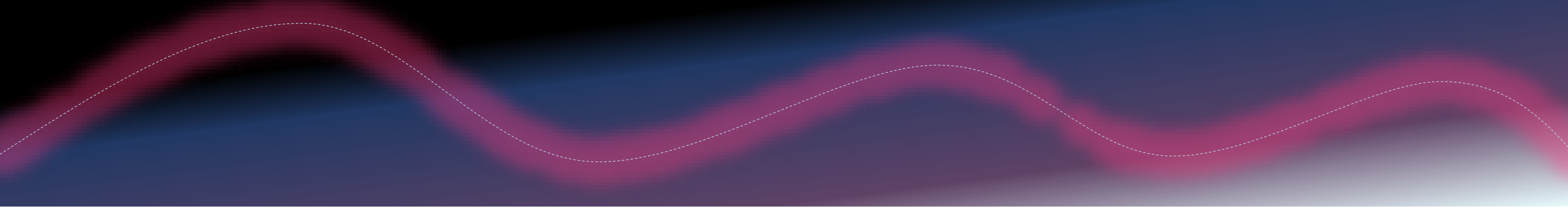

Poster 01

EFFICIENCY ENHANCEMENT TECHNIQUE FOR FREE ELECTRON LASER

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Keywords: ***Free-Electron Laser (FEL), Undulator, Efficiency, Undulator, Wiggler***

ABSTRACT

A Free Electron Laser (FEL) is a Fourth-generation light source that emits incredibly bright and brief radiation pulses. Many aspects of how a Free Electron Laser works and operates are similar to those of a laser, except instead of employing stimulated emission from atomic or molecular excitations as a Gain medium, it uses relativistic electrons. A group of electrons moving through a magnetic structure produce radiation (Called Undulator or wiggler). This radiation is further amplified in a FEL as it interacts with the electron bunch again, causing the electrons to begin emitting coherently and allowing an exponential rise in the total radiation intensity. In this research, we examine two major ways in which we can enhance the efficiency of a Free Electron Laser. Namely the undulator tapering and the phase jump method. Undulator tapering is a well-known technique for improving the performance of free-electron lasers. It functions by maintaining the resonant wavelength constant despite variations in the energy of the electron beam. Using this method, the FEL's spectrum brightness and energy-extraction efficiency can both be increased. The phase jump technique can enhance a free electron laser's efficiency. The technique makes use of the phase-chicanes in the drift segments in between the undulating segments. By applying appropriate phase jumps, the microbunched electron beam can decelerate and radiate coherently beyond the initial saturation, enabling further energy transfer to the optical beam.

References

[1] Margaritondo, G.; Rebernik Ribic, P. (2011-03-01). "A simplified description of X-ray free-electron lasers". Journal of Synchrotron Radiation. **18** (2): 101–108. doi:10.1107/S090904951004896X. ISSN 0909-0495. PMC 3042323. PMID 21335894.

[2] ^ Huang, Z.; Kim, K. J. (2007). "Review of x-ray free-electron laser theory" (PDF). Physical Review Special Topics: Accelerators and Beams. **10** (3): 034801. Bibcode:2007PhRvS..10c4801H. doi:10.1103/PhysRevSTAB.10.03480

Poster 02

Mechanochromic polymers for mechanical strain/stress sensors

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Keywords: Mechanochromism, Photochromism, Polymers, Naphthopyran

The detection of mechanical stresses is a major challenge to controlling the evolution of the mechanical properties of a material and detecting fractures or deformations. This would be particularly useful in the fields of transport, construction, security, and packaging. [1]

Organic mechanochromophores are molecules that change their absorption and/or emission wavelength upon being subjected to mechanical stress. Covalent incorporation of these mechanophores into polymer matrices can result in useful polymeric materials sensitive to stress/strain. Recently, several photochromic molecules have found their applications as mechanochromophores when incorporated into the polymer matrix. The labile bonds in the photochromic molecules are broken by exposure to UV light and result in an isomer accompanied by a color change. Recent studies show that these labile bonds can also be broken by mechanical force. Isomerization-based photochromes such as spiropyran (SP), naphthopyran (NP) are one of the common types of molecules that can also act as mechanochromophores.[2–4]

Most of the mehcanochromic polymer exhibit only a single chromatic change as a response to mechanical stimuli. Here we are presenting our efforts towards the design and synthesis of multistage mecahnochromophores with photochromes which consist of two napthopyran units conjoined with the same core. These molecules consist of a spiro-junction that undergoes ring-opening under external force, resulting in resonance structures causing a color change. These molecules can exhibit multi-stage photochromism response under UV and visible light due to the presence of two photochromic units in conjugation. The study of bond-breaking mechanisms and the incorporation of these mechanochromophores into a range of polymer matrices for stress/strain sensing is also carried out.

[1] Stuart et al, *Nature Mater* **2010**, *9*, 101–113.
[2] Robb et al, *J. Am. Chem. Soc.* **2016**, *138*, 12328–12331.
[3] Inagaki et al., *Photochem. Photobiol. Sci.* **2018**, *17*, 946–953
[4] McFadden et al., *J. Am. Chem. Soc.* **2019**, *141*, 11388–11392.

Poster 03

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

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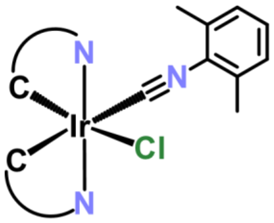
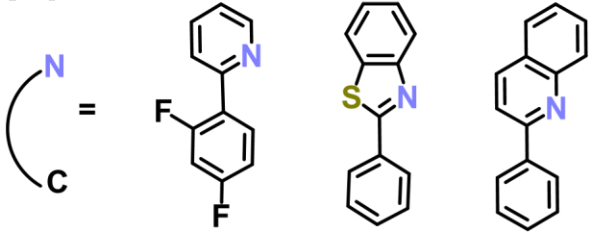
Keywords: Phosphorescence, Iridium(III) complexes, Cyclometalated, Isocyanide, Acetylide

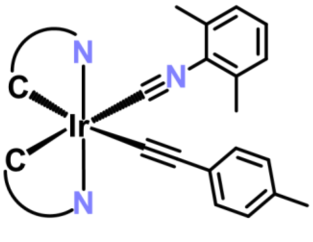
Over the last few decades, luminescent d^8 Pt(II) and d^6 Ir(III) metal complexes have received expanding interest due to their potential application for optoelectronic fields. In particular, cyclometalated Ir(III) complexes display very high photophysical performances due their good photostability, high photoluminescent quantum yields (Φ_{PL}), facile color tunability and long-lived triplet excited states. As a result of such properties, these complexes are used in different files of applications such as phosphorescent dopants in organic light-emitting diodes (OLEDs), lightemitting electrochemical cells (LEECs), solar cells (DSSCs- dye-sensitized solar cells), multifunctional devices (OLETs -organic light-emitting transistors) and photoredox catalysis [1]. These complexes usually display mixed metal-to-ligand charge transfer/ligand centered (^{3}MLCT/^{3}LC) excited states with some ligand-to-ligand charge transfer (^{3}LLCT) character depending on the auxiliary ligands. In this context, the coordination of strong field ligands such as CN^-, isocyanide or acetylide is desirable because they rise the energy of the *dd* metal centered causing enhancement of the quantum yields.

Following our interest aiming in designing photoluminescent complexes featuring isocyanide and/or acetylide ligands [2, 3], here we present the synthesis of a new family of iridium cyclometalated heteroleptic complexes [Ir(C^N)$_2$(CNXyl)(C□CR)] (R= *p*-tolyl **a**; $C_6H_2(OMe)_3$ **b**; pyrene **c**), which have been synthesized using the corresponding chloride/CNXyl complexes [Ir(C^N)$_2$Cl(CNxyl)] [C^N = difluorophenylpyridinate (dffpy) **1**; 2phenylbenzothiazolate (pbt) **2**; 2-phenylquinolate (pq) **3**] and (AgC□CR)$_x$ as precursors. All complexes have been fully characterized and their luminescent properties evaluated in several media.





dfppy 1 **pbt 2** **pq 3**



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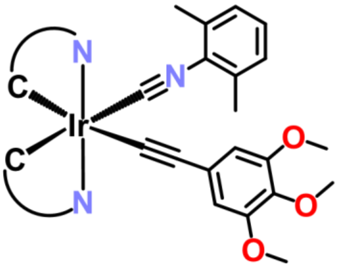

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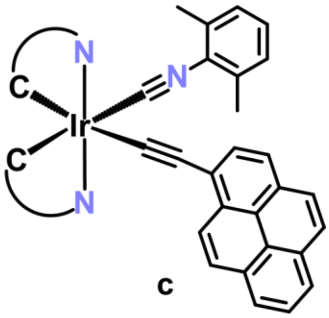

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[1] Feng, Z.; Sun, Y.; Yang, X.; Zhou, G. *Chem. Rec.* **2019**, *19*, 1710-1728.

[2] Fernández-Cestau, J.; Giménez, N.; Lalinde, E.; Montaño, P.; Moreno, M. T.; Sánchez, S. *Organometallics* **2015**, *34*, 1766-1778. [3] Martínez-Junquera, M.; Lara, R.; Lalinde, E.; Moreno, M. T. *J. Mater. Chem. C* **2020**, *8*, 7221-7233

Poster 04

INFLUENCE OF ZEOLITE CHARACTERISTICS ON PHOTOPOLYMERIZATION OF ZEOLITE/POLYMER BASED COMPOSITES

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Keywords: composites, zeolite, photopolymerization, 3D printing, nano particles

3D printing provides possibility for the preparation of structured zeolite monoliths, which can overcome the drawback of limited forms obtained from conventional shaping methods and make more efficient use of this material [1] [2]. Compared to other techniques, photopolymerization presents many advantages such as environment friendly, low energy consumption and excellent spatial and temporal control. Nevertheless, photocurable system with fillers still faces its challenge for the light penetration issue (Figure 1). In this study, the effect of different characteristics of LTA zeolite (crystal size, molar Si/Al ratio) are discussed. The results demonstrate that the nano-sized particles lead to the better depth of cure (DOC), optical properties and mechanical properties for the composites compared to micro-fillers. Furthermore, Si/Al ratio of LTA zeolites under study (1 □ Si/Al □ 2.8) also has an impact on the optical property and photopolymerization kinetics. This work enables a better understanding towards the fabrication of zeolite/polymer based composites by photopolymerization and will expand the potential applications for 3D printing and zeolite shaping.

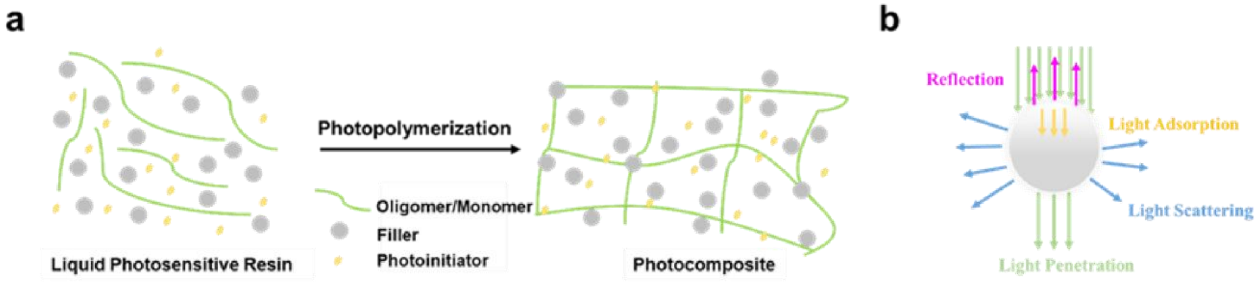

Figure 1. a) Curing process of the filled photopolymer; b) optical losses due to filler particles.

[1] GAO, Yuanyuan, ZHANG, Yijun, MICHELIN, Laure, et al. Binder effects in photopolymerized acrylate/zeolite composites for 3D printing/ionexchange applications. Materials Chemistry and Physics, 2023, vol. 293, p. 126853.

[2] ZHANG, Yijun, GAO, Yuanyuan, MICHELIN, Laure, et al. Photopolymerization of ceramic/zeolite reinforced photopolymers: Towards 3D/4D printing and gas adsorption applications. European Polymer Journal, 2022, vol. 179, p. 111552.

Poster 05

SYNTHESIS AND PHOTOPHYSICAL INVESTIGATION OF TRIPHENYLAMINE-BODIPY PHOTOSENSITIZERS

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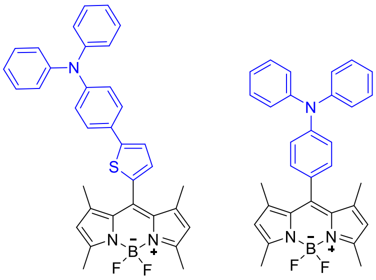
Keywords: BODIPY, Photosensitizers, Photophysics, D−□−□ molecules, Synthesis

The emergence of photodynamic therapy (PDT) has introduced a new path for cancer treatment, due to the high toxicity to cancer cells, low biological damage and controllable characteristics of singlet oxygen generation [1]. The versatility of the BODIPY structure, from synthesis to physicochemical properties, makes it a versatile building block to develop efficient photosensitizers for PDT. The majority of reported BODIPY photosensitizers are currently of the halogen-substituted type [2]. However, the introduction of heavy atoms, in general, leads to photosensitizers with higher cell cytotoxicity and reduced cell compatibility. Thus, there is an urgent need to develop novel photosensitizers that do not require heavy atom substitution. Triphenylamine-BODIPY□-conjugated molecules with typical D–A configuration have been used for studying aggregationinduced emission (AIE), as well as their charge transfer (CT) excited state properties[3]. Having in mind the work developed in our research group, concerning BODIPY derivatives for several optical and biological applications,[4-6] we report the design and synthesis of D-A triphenylamine-BODIPY molecules **1**-**2** (Figure 1), in order to study the influence of the addition of a thiophene spacer in the spectroscopic and photophysical properties, as well as to evaluate their singlet oxygen sensitization efficiencies. Triphenylamine-BODIPY derivatives **1**-**2** were synthesized by the Lindsey´s method [4-6]. The photophysical study comprised the electronic absorption, steady-state and time-resolved fluorescence data together with pump-probe transient absorption spectroscopy to characterize the photoinduced dynamics of BODIPYs **1**-**2** from the femtosecond to the microsecond time scale. In toluene solution a significant reduction in the fluorescence quantum yield and concomitant increase in the triplet formation quantum yield (estimated from the efficient singlet-oxygen sensitization quantum yield) was observed with the introduction of the thiophene spacer. Moreover, in mixtures of good and poor solvents (THF:water mixtures) aggregation-caused fluorescence quenching was observed for the investigated BODIPYs.



1 **2**

Figure 1. Structures of the investigated BODIPY derivatives.

[1] Gunaydin, G.; Gedik, M. E.; Ayan, S. Front. Chem., **2021**, 9, 686303.
[2] Gorbe, M.; Costero, A. M.; Sancenón, F.; Martínez-Máñez, R.; Ballesteros-Cillero, R. Dyes and Pigments, **2019**, 160, 198-207.
[3] Hu, R.; Lager, E.; Aguilar-Aguilar, A.; Liu, J.; Lam, J. W. Y.; Sung, H. H. Y.; Williams, I. D.; Zhong, Y.; Wong, K. S.; Peña-Cabrera, E.; Tang, B. Z. J. Phys. Chem. C, **2009**, 113, 15845–15853.
[4] Gonçalves, R.C.R.; Pina, J.; Costa, S.P.G.; Raposo, M.M.M. Dyes Pigm. **2021**, 196, 109784.
[5] Lo Presti, M.; Martínez-Máñez, R.; Ros-Lis, J. V.; Batista, R. M. F.; Costa, S. P. G.; M. Raposo, M. M.; Sancenón, F. N. J. Chem. **2018**, 42, 78637868.
[6] Collado, D.; Casado, J.; González, S. R.; Navarrete, J. T. L.; Suau, R.; Perez-Inestrosa, E.; Pappenfus, Ted. M.; Raposo, M. M. M. Chem. Eur. J. **2011**, 17, 498 – 507.

Poster 06

DYE PHOTODEGRADATION WITH ORGANOMETALLO-TITANIA HYBRID MATERIALS USING VISIBLE LIGHT

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Keywords: titania, photocatalytic dye degradation, visible light, organometallo-titania, nanoestructured.

Titanium dioxide (TiO_2) is an actually promising material due to its wide variety of applications – i.e. in photocatalysis and solar cells design. However, it has some drawbacks due to the high electronic hopping between the valence and conduction bands (bandgap) of any of its polymorphs (of about 3.2 eV). To solve this problem and get visible-light active titania, our group has delved an *in-situ* method based on *Sol-Gel Coordination Chemistry* [1] (*Figure 1.A*). For this purpose, two nanostructured organometallo-titania hybrid materials, **[1]-TiO_2** and **[2]-TiO_2**, have been synthesized from two Ir(III) complexes: $[Ir(ppy)_2(3,3'\text{-}H_2dcbpy)](PF_6)$ (**1**)[2] and $[Ir(ppy)_2(4,4'H_2bicinchoninic)](PF_6)$ (**2**), respectively. These materials have proven to be very stable and effective photocatalysts under visible-light irradiation in the degradation of a standard dye such as Rhodamine 6G in aqueous media. Both hybrid materials are much more efficient photocatalysts than a related standard titania (**TiO_2**). Under blue-light illumination and room temperature, **[1]-TiO_2** shows higher kinetic constants than **[2]-TiO_2**; although in both cases, similar percentages of degradation are finally obtained (*Figure 1.B*). Therefore, they can be used in future wastewater purification applications, thus contributing to the environmental benefit.

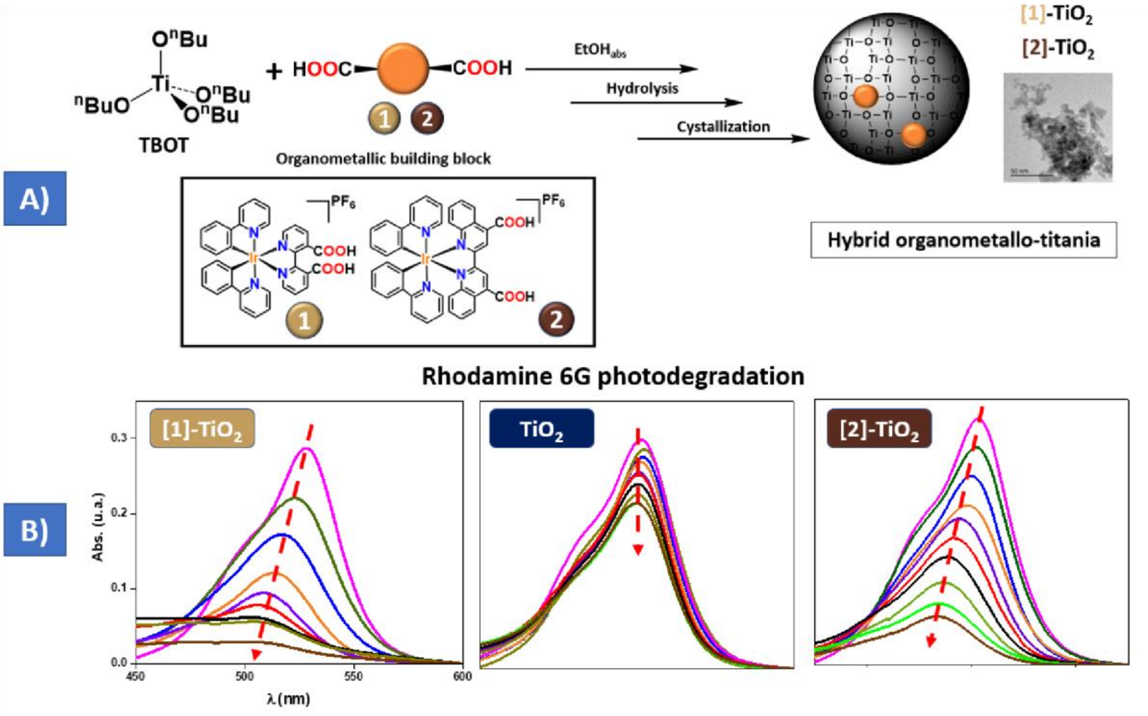

Figure 1. A) *In-situ* hybrid materials obtained by *Sol-Gel Coordination Chemistry*. B) Rhodamine 6G photodegradation using the nanoestructurated materials under blue-light LED illumination.

[1] M. Rico-Santacruz, Á. E. Sepúlveda, E. Serrano, E. Lalinde, J. R. Berenguer, J. García-Martínez. J. Mater. Chem. C, **2014**, 2, 9497.

[2] M. Rico-Santacruz, Á. E. Sepúlveda, C. Ezquerro, E. Serrano, E. Lalinde, J. R. Berenguer, J. García-Martínez. Appl. Catal. B. **2017**, 200, 93-105.

Poster 07

Excited State Dynamics of near-IR Dyes Designed for Transparent Solar Cells

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Keywords: Dye-sensitized solar cells, Femtosecond Transient Absorption

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 quasi-transparent devices designed for Building 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 dye, named TB202, in solution phase as well as incorporated in complete prototype devices of operating TiO_2 and of the non-productive high bandgap semiconductor (SC) Al_2O_3, as a reference.

Due to thienyl substitutions TB202 (see figure panel C) exhibits a strong redshifted absorption band peaking at 790 nm (ε >100,000 $M^{-1}cm^{-1}$) 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 (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 electron injection into TiO_2[4]. VIS/near-IR ultrafast spectroscopy has been performed to investigate the loss channels as a function of the co-adsorbent CDCA concentration, which was added to reduce the dye-aggregation in the DSSCs.

Using this method, we have identified the excited state absorptions (ESAs), which belong to the monomers, the aggregates and the monomer cation photoproduct, and the kinetic rates related to the productive monomer-tosemiconductor charge transfer (CT) and ET. The results show, that the charge transfer for TB202 is as slower than in previously studied TB dyes[4], and on the same timescale as ET even at the highest CDCA concentration. This is consistent with a lower driving force for the carrier injection, the energy difference between the monomer excited state and the TiO_2 conduction band edge, as compared to TB207.

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

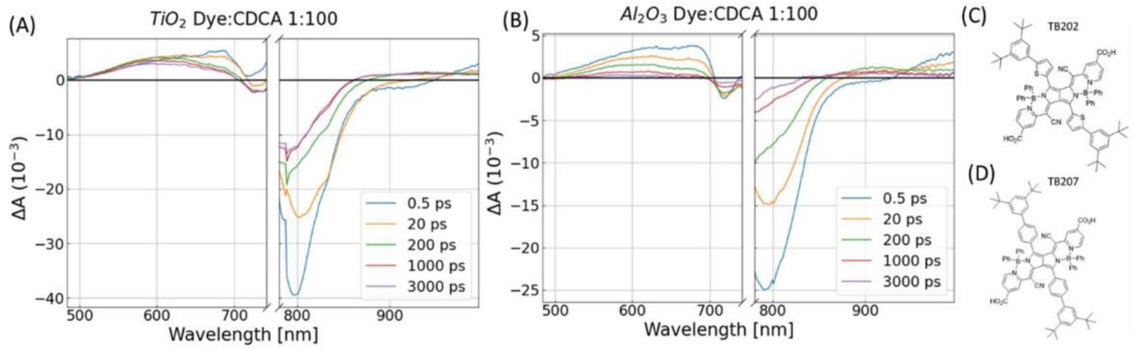

Figure 1. Transient absorption spectra of prototype cells based on TB202 mixed 1:100 with CDCA on TiO_2 (A) and on Al_2O_3 photoanode (B) as a reference. The spectra are shown at different pump-probe delays. At this CDCA concentration aggregate formation is reduced (880-930 nm) at 200 ps, panel (B). ESA of the monomers and the cations, appear to be overlapping in the VIS (500-700 nm) at early times, but cation absorption dominates for > 200 ps (panel A) without any apparent decay. In the NIR regime (>850nm) the cation absorption is flat (870-1000 nm, ≥200 ps). The chemical structures of TB202 and TB207 is displayed on panel C and D respectively.

[1] T. Geiger et al., Int. J. Photoenergy, 2014, e258984

[2] S. Kuster et al., Dyes & Pigments, 2010, 87, 30

[3] G. M. Fischer, et al., Angew. Chemie, 2011, 50, 1406-1409.

[4] T. Baron et al., Angew. Chem. Int. Ed. 2022, 61, e202207459

Poster 08

Synthesis of photoswitchable carbohydrate-based macrocycles as chiral dopants for liquid crystals

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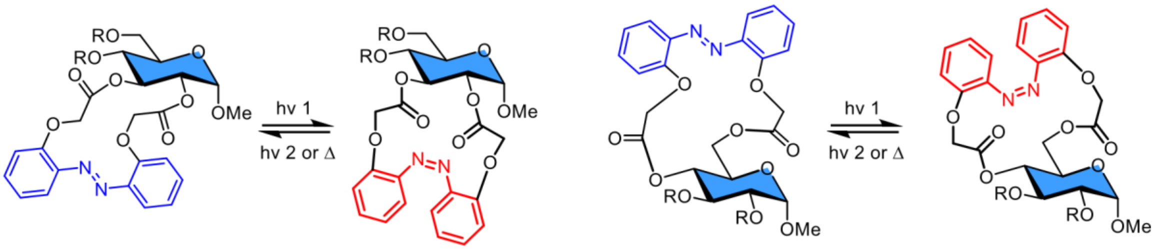
Keywords: photoswitch, glycomacrocycle, chiral dopant, liquid crystal

Glycomacrocyclic compounds are interesting molecules because of their natural existence, their interesting biological, physicochemical properties, and potential applications in various fields.[1] Photoswitchable molecules such as azobenzene can be reversibly isomerized by light into isomers featuring different structural and electronic properties.[2] Photoresponsive liquid crystalline (LC) system has attracted considerable interest to a very promising area of soft photonics and mechanics.[3] Under light irradiation, it is possible to modulate or switch the orientation of LC molecules to achieve desired optical and mechanical properties of this system remotely and selectively. Photo-tunable self-organized helical superstructures of cholesteric liquid crystals (CLCs) have shown promising results. Its helical orientation and pitch length can be dynamically light-controlled enabling the practical photonic applications. The most convenient and economical approach to obtain CLCs is to add a chiral dopant into a commercially available achiral nematic liquid crystal host at the appropriate concentration to induce selective reflection in the wavelength of interest.[4] We have demonstrated the promising properties of azobenzene-derived glycomacrocycles as chiral dopants in providing dynamic control of helical superstructures in response to light stimulus.[5]

In this project, we decide to develop photoswitchable glycomacrocycles containing azobenzene and natural carbohydrate which are linked at 2, 3 or 4, 6 positions of carbohydrates to take advantage of their natural chirality to induce a chirality transfer from the sugar to the azobenzene moiety. By introducing different R groups on 2, 3, or 4, 6 positions of the carbohydrate (Scheme), we will explore their influence in LC system. The synthetic approaches to these glycomacrocycles will be presented.



R = H, C_6H_{13}, Ac, $C_5H_{11}CO$

Scheme: Structures and photoisomerization of target photoswitchable glycomacrocycles.

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[1] J. Xie, N. Bogliotti, *Chem. Rev.* **2014**, *114*, 7678-7739.
[2] A. A. Beharry, G. A. Woolley, *Chem. Soc. Rev*. **2011**, *40*, 4422-4437.
[3] L. Wang, Q. Li, *Chem. Soc. Rev*. **2018**, *47*, 1044-1097.
[4] Y. Kim, N. Tamaoki, *ChemPhotoChem.* **2019**, *3*, 284-303.
[5] Y. Kim, N. Mafy, S. Maisonneuve, C. Lin, N. Tamaoki, J. Xie, *ACS Appl. Mater. Interfaces* **2020**, *12*, 52146-52155.

Poster 09

PHOTOACTIVE N-HETEROCYCLING CARBENE COMPLEXES FOR BONDFORMING PHOTOCATALYSIS

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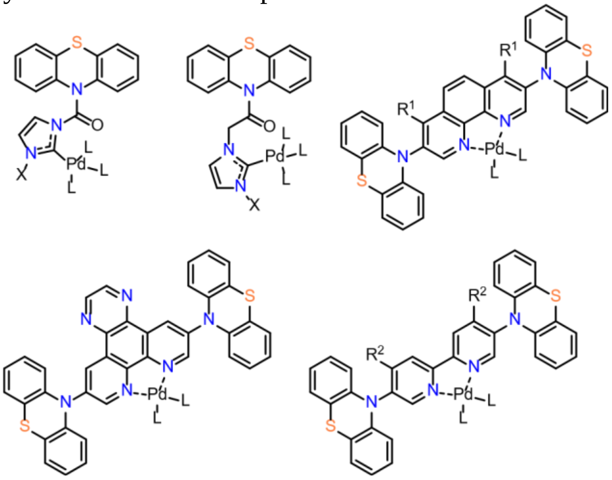
Keywords: Photocatalysis, N-heterocycling carbene complexes, Pd catalysis, visible light

Pd catalyzed reactions of C-N and C-C bond formation play a significant role in the production of both pharmaceuticals and functional materials. Despite their widespread use, they also require high temperatures and high metal catalyst loads, which greatly reduce the environmental and energy efficiency of the reaction. The combination of photocatalysis with transition metal catalysis is a powerful tool for performing complex chemical transformations under environmental conditions, and it also allows reducing the amount of metal catalyst by regenerating it with photocatalyst[1].

The design of the new catalytic system containing a photoactive block and transition metal allows reactions to be carried out at room temperature and reduces the amount of expensive Pd needed for the reaction, as well as increasing the number of catalytic cycles without loss of efficiency. The use of the dual catalytic system also increases the yield and selectivity in reactions for complex and non-activated substrates.



Scheme 1. Compounds for single-component Pd/photoredox catalysis

The synthesized complexes proved to be suitable as a metallic photocatalyst in photocatalytic amidation (C-N bond formation) and arylation (C-C bond formation) reactions. Further variation of the structure of the photoactive block and analysis of its influence on the properties of molecules will undoubtedly influence the development of new photocatalytic systems.

[1] Twilton, J., Le, C., Zhang, P., Shaw, M.H., Evans, R.W., MacMillan, D.W.C. Nat. Rev. Chem., **2017**, 1, 0052.

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