

ITALIAN PHOTOCHEMISTRY MEETING *2021*

16-18 DECEMBER 2021
TORINO

BOOK OF ABSTRACTS

Con il patrocinio di:



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Programme – Thursday 16th December 2021

Department of Chemistry, Aula Magna

13:00-14:00	Registration		
14:00-14:15	Loredana Latterini GIF President	Opening Remarks	Chair: Andrea Fin University of Torino
	Session 1 Honorary Invited Speaker	Chair: Mirco Natali University of Ferrara	Co-chair: Marco Minella University of Torino
14:15-15:00	Elio Giamello University of Torino	Photochemistry and Photocatalysis of Visible Light Active (VLA) Solids	
15:00-16:00	Short and Flash Oral Communication		
OC-01	Brunella Bardi Oral Communication (online)	Mean-Field Effects on the Phosphorescence of Dinuclear Re(I) Complex Polymorphs	
OC-02	Valentina Ferraro Oral Communication	Green-Emitting Tetrahedral Mn(II) Complexes with [O=P]-Donor Ligands	
OC-03	Davide Vione Oral Communication	A Monochromatic Approximation for Environmental Photochemistry	
FC-01	Giuseppe Nocito Flash Communication	Photochemical Route to CDs-Au Nanohybrid for Photothermal Applications	
FC-02	Francesca Laneri Flash Communication	Biofriendly Route to Gold Nanoplasmonics through Mixed Cyclodextrin Branched Polymers Photoreleasing Nitric Oxide	
FC-03	Andrea Fermi Flash Communication	Isophthalonitrile Derivatives as TADF-Active Chromophores for Metallaphotoredox Catalysis	
FC-04	Elena Cambiotti Flash Communication	Thermal Control of Up-Conversion Process on Silica Capsules through Incoherent Excitation	
16:00-16:30	Break		
	Session 2 GIF Award Keynote Speaker	Chair: Francesco Nastasi University of Messina	Co-chair: Polyssena Renzi University of Torino
16:30-17:00	Alessio Cesaretti GIF Young Investigator Awards 2021	Ultrafast Dynamics in Micro-Heterogeneous Organized Systems: Exploiting Photophysics for Medium Characterizations and Biomedical Applications	
17:00-18:00	Short and Flash Oral Communications		
OC-04	Elena Bassan Oral Communication (online)	The Quest for Triplet Population and Reducing Ability in Organic Photoredox Sensitizers: the Case of BODIPY Dyes	
OC-05	Federica Minuto Oral Communication	Ketene 3-Component Staudinger Reaction (K-3CSR): a Novel Photoinduced Approach to the Synthesis of β -Lactams	
OC-06	Alexandra Jorea Oral Communication	Photocatalyzed Functionalization of α,β -Unsaturated Carboxylic Acids	
OC-07	Andrea Cosola Flash Communication	Multi-Photoactive BAPO-Cyclodextrin: a Two-in-One Photoinitiator and Photocrosslinking Agent	
FC-05	Lorenzo Casimiro Flash Communication	Dimethylazobenzene: A New Chemical Actinometer	
FC-06	Lorenzo Di Terlizzi Flash Communication	Visible Light-Driven Synthesis of Symmetrical (Hetero)Biaryls by Homocoupling of Arylazo Sulfones	
FC-07	Emanuele Azzi Flash Communication	Visible Light Driven Cyclization for the Synthesis of 2-Functionalized Saturated N-Heterocycles	
18:30-20:00	Welcome Aperitive Caffetteria dell'Università		

Programme – Friday 17th December 2021

Department of Chemistry, Aula Magna

	Session 3 Keynote Speaker	Chair: Maurizio Fagnoni University of Pavia	Co-chair: Nadia Barbero University of Torino
9:30-10:00	Marina Freitag Newcastle University	Diffuse Light Harvesting to Structured Information	
10:00-11:15	Short and Flash Oral Communications		
OC-08	Bas de Jong Oral Communication	Charge Recombination Dynamics: an Experimental Approach from Perovskite-based Devices to Luminescent Solar Concentrators	
OC-09	Natalie Flores-Diaz Oral Communication	Photopolymerization of Hyperbranched Networks by Thiol-ene “Click” Reaction in Cobalt-Based Electrolytes for Dye-Sensitized Solar Cells	
OC-10	Ambra Maria Cancelliere Oral Communication	Metal-Based Photosensitizers and Catalysts for Light-to-Energy Conversion	
OC-11	Edoardo Marchini Oral Communication	A Series of Iron(II)-NHC Sensitizers with Remarkable Power Conversion Efficiency in Photoelectrochemical Cells	
OC-12	Daniele Veclani Oral Communication	Interaction of a TiO ₂ Surface with Organophosphonic Acids: the Role of pH	
FC-08	Giorgio Volpi Flash Communication	Emissive Imidazo[1,5-a]Pyridine Scaffold: Luminescent and Versatile Core for Various Applications	
FC-09	Annalisa Polo Flash Communication (online)	Multifaceted Role of Mo ⁶⁺ Doping in BiVO ₄ Photoanodes for Solar Energy Conversion	
11:15-11:45	Break		
	Session 4 Invited Speaker Plenary	Chair: Claudia Barolo University of Torino	Co-chair: Lucia Fagiolari Polytechnic University of Torino
11:45-12:30	Ruben D. Costa Technical University of Munich	Bio-Phosphors for Bio-Hybrid Light-Emitting Diodes	
12:30-13:00	Short and Flash Oral Communications		
SC-01	Cicci Research Sponsor Communication		
OC-13	Giulia Quaglia Oral Communication	Utilizing Upconversion via Triplet-Triplet Annihilation for Radiation Modulation and Optical Communication Experiments	
FC-10	Matteo Cingolani Flash Communication	Micro- and Nanoplastics: Detection in Water with a Fluorogenic Hyaluronan Probe	
13:00-14:30	Lunch Pina's Kitchen		
14:30-15:30	City Sightseeing Tour Bus Tour		
	Session 5 GIF Award Keynote Speaker	Chair: Sebastiano Campagna University of Messina	Co-chair: Matteo Bonomo University of Torino
15:30-16:00	Francesco Pellegrino GIF Young Investigator Award 2021	A New Strategy for Overcoming the Volcano in Water Photosplitting: Controlled Periodic Illumination	
16:00-17:20	Short and Flash Oral Communications		
OC-14	Alberto Bianco Oral Communication	Direct NAD(P)H Regeneration Using Light: a Novel Application of an Old Compound	
OC-15	Cristina Parisi Oral Communication	A Doxorubicin-NO Releaser Molecular Hybrid Activatable by Green Light to Overcome Resistance in Breast Cancer Cells	
OC-16	Tommaso Bianconi Oral Communication	An Insight into the Excited-State Deactivation Mechanism of New Aggregation-Induced Emission Materials for Biological Applications and Optoelectronics	
FC-11	Jessica Groppi Flash Communication	The Evolution of Light Effected Autonomous Molecular Pumps	

FC-12	Brian Sachini Flash Communication	Improving Light-Driven Molecular Pumps: Dissecting Thermodynamic and Kinetic Entanglement in a Photoswitchable Molecular Axle
FC-13	Stefano Corrà Flash Communication	Dynamic and Thermodynamic Insights in the Operation of a Light-Fueled Supramolecular Pump
FC-14	Marco Villa Flash Communication	Thiospherulene: Polysulfurated and Phosphorescent Molecular Cage
FC-15	Antonio Fiorentino Flash Communication	Acidochromism of First-Generation Donor-Acceptor Stenhouse Adducts (DASAs): a pH-Sensitive Switch in Halogenated Solvents
FC-16	Leonardo Andreoni Flash Communication	Calix[6]arene-Based Rotaxane Orientational Isomers with Distinct Photophysical Properties
FC-17	Letizia Mencaroni Flash Communication	Singlet Fission Footprints in a New Class of Fluorene Derivatives: Charge-Transfer Mediation and Possible Implications
17:20-18:40	Division Assembly	
20:00	Social Dinner "Ristorante La Badessa"	

Programme – Saturday 18th December 2021

Department of Chemistry, Aula Magna

	Session 6 Invited Speaker Plenary, GIF Award Keynote Speaker	Chair: Serena Silvi University of Bologna	Co-chair: Ivana Miletto University of Eastern Piedmont
9:00-9:45	Aldo Romani University of Perugia	Photophysics and Photochemistry for Beauty	
9:45-10:15	Sara Angeloni Premio "Ugo Mazzucato" per la migliori tesi di dottorato in fotochimica 2021	Silicon Nanocrystals Tailored for Bioimaging and Energy Conversion	
10:15-11:15	Short and Flash Oral Communications		
OC-17	Sara Bonacchi Oral Communication (online)	Tunable Near-Infrared Emitting Nanoclusters: an In-situ Spectroelectrochemical Fluorescence Study	
OC-18	Bejoy Mohandas Kochan Sathyaseelan Oral Communication	3-Oxidopicolinate: A Surprising Short Bridge for Generating Bright Phosphorescence from Binuclear Iridium(III) Complexes	
OC-19	Arianna Menichetti Oral Communication	Local Light-controlled Generation of Calcium Carbonate and Barium Carbonate Biomorphs via Photochemical Stimulation.	
OC-20	Liviana Mummolo Oral Communication	Supramolecular-Based Fluorescent Ligands as Sensing Tools for the Detection of Emerging Pollutants	
OC-21	Matteo Caprioli Oral Communication	PVA-Based DLP- 3D Printed Self-Healing Hydrogels	
11:15-11:45	Break-Poster Session		
	Session 7 Awards and Closing remarks	Chair: Loredana Latterini GIF President	Co-chair: Andrea Fin University of Torino
11:45-12:30	Award Ceremony		
12:30-12:45	Closing Remarks		

Plenary Lecture

Photochemistry and Photocalysis of Visible Light Active (VLA) Solids

Elio Giamello^a

^a *Dipartimento di Chimica, Università di Torino.*

Photocatalytic processes aim to exploit the energy of light to promote chemical transformations. This scope can be pursued in various applications including pollution remediation (total oxidation of pollutants), solar fuels production (e.g. water photosplitting and CO₂ reduction) and, more generally, in all types of chemical processes in which the required thermal energy can be replaced by electromagnetic energy.

A standard process in heterogeneous photocatalysis is based on the photoexcitation of a suitable semiconducting system inducing the promotion of electrons in the conduction band (CB) and the formation of electron-holes (holes, h⁺) in the valence band (VB). The reductive and oxidative capacities of these photoexcited charge carriers respectively depend, as a first approximation, on the chemical potentials of CB and VB. The materials that have so far dominated the field of environmental photocatalysis are based on titanium dioxide or other semiconductors with high band gap, whose excitation requires the use of UV radiation. In recent years an intense effort has been devoted to the search for innovative photocatalytic systems capable of working under visible light illumination. The approaches followed to this aim include the use of: i) small band gap semiconductors such as C₃N₄; ii) semiconducting systems with band gap modified by the insertion of impurities; iii) coupled semiconductors reproducing either the so-called Z scheme of natural photosynthesis. In the present contribution we will report about our experimental action that is devoted to individuate and prepare heterogeneous systems possibly active in visible light (VLA systems). Our work is based on a knowledge-based approach aiming to unravel the main phenomena occurring in a solid and at its interface. Electron Paramagnetic Resonance spectroscopy plays a fundamental, though not unique, tool in our activity. Different topics will be discussed including: i) photochemistry under visible light of wide gap pristine oxides; ii) photochemistry of oxides doped with rare earth ions; iii) systems based on oxide-oxide heterojunctions.

In the case of water photosplitting reactions the role of co-catalyst for hydrogen evolution (HER) based on earth abundant elements will be also mentioned.

[1] M. Chiesa, E. Giamello, S. Livraghi, M.C. Paganini, V. Polliotto, E. Salvadori, *Journal of Physics Condensed Matter*, 2019, *31*, 44400.

[2] M. Chiesa, S. Livraghi, M.C. Paganini, E. Giamello, E. Salvadori, *Chemical Science*, 2020, *11*, 6623.

[3] M.C. Paganini, E. Cerrato in *Materials Science and Photocatalysis*, E.I. Garcia-Lopez, L. Palmisano Eds, 2021, Chapter 14, 221.

Plenary Lecture

Bio-phosphors for Bio-Hybrid Light-emitting Diodes

Rubén D. Costa^a

^a *Technical University of Munich, Chair of Biogenic Functional Materials, Schulgasse, 22, 94315 Straubing, Germany.*

Bio-phosphors have emerged as an alternative to rare-earth color down-converting filters in light-emitting diodes (LEDs). They are mainly produced with biogenic emitters, like Fluorescent Proteins (FPs), embedded in polymer matrices.[1–3] The first bio-hybrid LED (Bio-HLED) with FP-phosphors featured a loss <10% of the emission intensity after 100 h.[1] This performance was recently enhanced using zero-thermal quenching PMMA-FP phosphors, reaching >150 days and 5 min of stability at low and high powers.[4] However, the ideal combination of highly efficient and stable fully biogenic phosphors is still in its infancy.[5] Here, we disclose the optimization of a new biopolymer hosting a stable eGFP mutant as green-emitting phosphor in Bio-HLEDs. The remarkable photoluminescent properties of the bio-phosphors - $\phi > 70\%$ - lead to Bio-HLEDs with excellent photo-stabilities > 230 h operating under high powers, representing 2 orders of magnitude enhancement. This represents a crucial breakthrough in the development of *in toto* bio-phosphors.

- [1] M. D. Weber, *et al. Adv. Mater.*, **2015**, *27*, 5493.
- [2] V. Fernández-Luna, *et al. Adv. Funct. Mater.*, **2019**, *29*, 1904356.
- [3] C. F. Aguiño, *et al. ACS Omega* **2018**, *3*, 15829.
- [4] A. Espasa, *et al. Nat. Commun.* **2020**, *11*, 867.
- [5] V. Fernández-Luna, *et al. Mater. Horizons* **2020**, *7*, 1790.

Plenary Lecture

Photophysics and Photochemistry for Beauty

Aldo Romani^a

^a *Centro di Eccellenza SMAArt, Department of Chemistry, Biology and Biotechnology, University of Perugia.*

Artworks can be cynically considered as a more or less complex assembly of several different materials so, a photophysical and photochemical approach to these objects could be considered similar to that daily used by any researcher who play with light and matter but considering a couple of differences: you are playing with extremely beautiful and, above all, priceless objects.

In this landscape, the photochemist's ability can play two meaningful roles in Cultural Heritage sciences; the first concerns friendly photophysical techniques such as absorption and emission spectroscopies applied as completely not invasive diagnostic tools in order to safely obtain materials' information from the precious objects. The second is the core of the photochemist's work that is the investigation and the comprehension of how and in which extent the light modifies physical-chemical properties of the materials contained in an artwork. Results obtained from investigations carried out on two masterpieces, the Munch's "Scream" exposed at the Munch Museum in Oslo [1,2] and Van Gogh's "The Olive Orchard" preserved at the National Gallery of Art in Washington DC [3,4], will be presented with the aim to highlight how both the photophysical and photochemical characterization of the materials used to produce figurative arts' treasures can provide absolutely necessary knowledge to conservators and restores who are called to preserve these "beauties" for the next generations.



[1] L. Monico, A. Chieli, S. De Meyer, M. Cotte, W. de Nolf, G. Falkenberg, K. Janssens, A. Romani, C. Miliani, *Chemistry – A European Journal*, **2018**, *24*, 11584.

[2] L. Monico, L. Cartechini, F. Rosi, A. Chieli, C. Grazia, S. De Meyer, G. Nuyts, F. Vanmeert, K. Janssens, M. Cotte, W. De Nolf, G. Falkenberg, I. C. A. Sandu, E. S. Tveit, J. Mass, R. P. de Freitas, A. Romani, C. Miliani, *Sci. Adv.*, **2020**, *6*, eaay3514.

[3] K.A. Dooley, A. Chieli, A. Romani, S. Legrand, C. Miliani, K. Janssens, J.K. Delaney, *Angew. Chem. Int. Ed.*, **2020**, *59*, 6046.

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GIF Young Investigator Awards 2021

Ultrafast Dynamics in micro-heterogeneous organized systems: exploiting photophysics for medium characterizations and biomedical applications.

Alessio Cesaretti^a

^a Department of Chemistry, Biology and Biotechnology and Centro di Eccellenza sui Materiali Innovativi Nanostrutturati (CEMIN), Via Elce di Sotto 8, 06123 Perugia, University of Perugia, Italy.

The close dependence of the photophysics of organic molecules on the experienced environment can serve a dual role of both probing the features of the surrounding medium, and revealing the properties of chromophores upon excitation and the fate of their excited states.

In my research activity, different organic molecules, including but not limited to solvatochromic push-pull dyes, have been investigated by resorting to femtosecond-resolved transient absorption and broadband fluorescence up-conversion spectroscopies, in homogeneous aqueous and organic solvents, as a function of acidity and polarity, [1-3] and in micro-heterogeneous environments of surfactant micelles and hydrogels, [4,5] as well as in deep-eutectic solvents.[6]

A series of cationic N-methyl pyridinium derivatives have been deeply studied: on the one hand, the inclusion in organized media allowed their excited-state dynamics to be rationalized and described by the formation of twisted intramolecular charge transfer states (TICT), [7] while the dependence of their fluorescence emission and excited-state dynamics on the local polarity and especially viscosity proved informative about the microenvironment provided by different organized media.[6]

These investigations have thus been instrumental in uncovering the structure/property relationships in push-pull dyes, [8,9] with the aim being to boost their NLO responses (*i.e.*, hyperpolarizability and two-photon absorption) in light of possible biomedical applications as theranostic agents. In this regard, the research also extended to more complex molecular structures in order to pursue desired features, *i.e.*, quadrupolar systems for their enhanced NLO properties, [10,11] and bis-cationic compounds, for their improved water-solubility.[12]

In fact, not only were found these molecules able to interact with biological targets inside the cell nuclei (*e.g.*, DNA and RNA), thus being cytotoxic, but also their two-photon excited fluorescence could be exploited for bioimaging purposes.[13] Moreover, the use of stimuli-responsive surfactant hydrogels allowed these systems to be characterized as possible drug carriers[14] and artificial glands[15] able to release their load where and when it is needed.

- [1] C. Bonaccorso, A. Cesaretti, F. Elisei, L. Mencaroni, A. Spalletti, C. G. Fortuna, *ChemPhysChem*, **2018**, 19(15), 1917. [2] A. Cesaretti, C. Bonaccorso, V. Carboni, M. S. Giubila, C. G. Fortuna, F. Elisei, A. Spalletti, *Dyes and Pigments*, **2019**, 162, 440. [3] B. Carlotti, A. Cesaretti, C. G. Fortuna, A. Spalletti, F. Elisei, *Physical Chemistry Chemical Physics*, **2015**, 17(3), 1877. [4] A. Cesaretti, B. Carlotti, C. G. Consiglio, T. Del Giacco, A. Spalletti, F. Elisei, *The Journal of Physical Chemistry B*, **2015**, 119(22), 6658. [5] A. Cesaretti, B. Carlotti, P. L. Gentili, R. Germani, A. Spalletti, F. Elisei, *Photochemical & Photobiological Sciences*, **2016**, 15(4), 525. [6] M. Tiecco, I. Di Guida, P. L. Gentili, R. Germani, C. Bonaccorso, A. Cesaretti, *Journal of Molecular Liquids*, **2021**, 331, 115718. [7] A. Cesaretti, B. Carlotti, R. Germani, A. Spalletti, F. Elisei, *Physical Chemistry Chemical Physics*, **2015**, 17(26), 17214. [8] B. Carlotti, A. Cesaretti, O. Cannelli, T. Giovannini, C. Cappelli, C. Bonaccorso, C. G. Fortuna, F. Elisei, A. Spalletti, *The Journal of Physical Chemistry C*, **2018**, 122(4), 2285. [9] A. Cesaretti, P. Foggi, C. G. Fortuna, F. Elisei, A. Spalletti, B. Carlotti, *The Journal of Physical Chemistry C*, **2020**, 124(29), 15739. [10] A. Cesaretti, A. Spalletti, F. Elisei, P. Foggi, R. Germani, C. G. Fortuna, B. Carlotti, *Physical Chemistry Chemical Physics*, **2021**, 23(31), 16739. [11] Y. Rout, A. Cesaretti, E. Ferraguzzi, B. Carlotti, R. Misra, *The Journal of Physical Chemistry C*, **2020**, 124(45), 24631. [12] L. Mencaroni, C. Bonaccorso, V. Botti, B. Carlotti, C. G. Consiglio, F. Elisei, A. Spalletti, A. Cesaretti, *Dyes and Pigments*, **2021**, 194, 109620. [13] V. Botti, A. Cesaretti, Ž. Ban, I. Crnolatac, C. G. Consiglio, F. Elisei, I. Piantanida, *Organic & biomolecular chemistry*, **2019**, 17(35), 8243. [14] A. Cesaretti, B. Carlotti, P. L. Gentili, C. Clementi, R. Germani, F. Elisei, *The Journal of Physical Chemistry B*, **2014**, 118(29), 8601. [15] A. Cesaretti, I. Di Guida, N. E. Caldero-Rodríguez, C. Clementi, R. Germani, P. L. Gentili, **2018**, *ACS Omega*, 3(12), 16777-16783.

Keynote Lecture

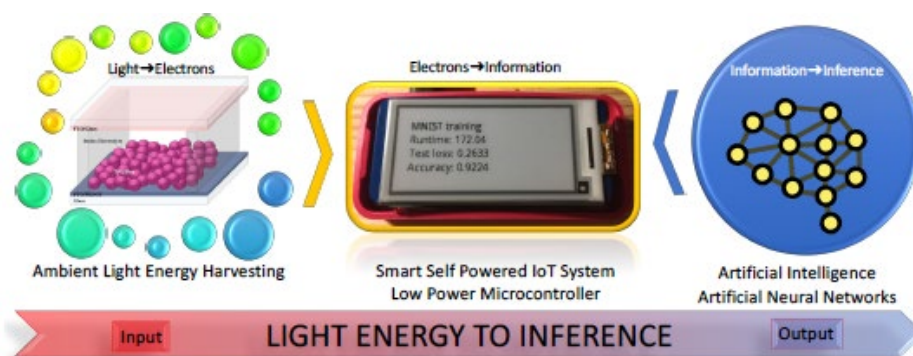
Diffuse Light Harvesting to Structured Information

Marina Freitag^a

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By 2025 about 75 billion IoT devices will be installed, of which the majority will reside indoors. It is therefore crucial to find an energy source that yields high efficiencies in this environment. At 34% efficiency under ambient light, while being more environmentally friendly, sustainable to produce and to recycle.[1–3] Dye-sensitized solar cells (DSCs) are known for efficient conversion of ambient light. Fast charge separation in a variety of organic dyes and tunable energy levels in Cu^{II/I} redox systems combined with negligible recombination processes allow DSCs to maintain a high photovoltage under ambient light. The co-sensitization of absorbers enables absorption over a broad spectral range and the adaption to most light sources.[4] As a result, DSCs outperform organic photovoltaics as well as silicon and thin-film GaAs technology under ambient lightning. We studied DSCs with Cu^{II/I}(tmby)₂ (tmby = 4,4',6,6'-tetramethyl-2,2'-bipyridine) electrolyte based on a combination of dyes XY1 and L1. The new dye sensitized “solar” cells achieve an unprecedented power output of 103.1 μW cm⁻² at 1000 lux.

The harvested “indoor” energy can be used to provide power to all crucial elements of IoT: communicate, sense and process. A major step forward was demonstrated as even machine learning and advanced image recognition is possible on these devices with the given energy for both learning and prediction. There is no need connect to an external power source or save energy (batteries) to prolong their lifetime, our system is designed to use all the available energy at any given time. Through thorough characterization, we can directly link the number of photons required for a computational inference: 2.72·10¹⁵ photons/inference. This is essentially the direct transformation of high entropy diffuse light into structured information. [5,6]



- [1] H. Michaels, M. Rinderle, R. Freitag, I. Benesperi, T. Edvinsson, R. Socher, A. Gagliardi, M. Freitag, *Chemical Science* **2020**, *11*, 2895–2906.
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- [3] M. Freitag, J. Teuscher, Y. Saygili, X. Zhang, F. Giordano, P. Liska, J. Hua, S. M. S. M. Zakeeruddin, J.-E. J.-E. M. Moser, M. Grätzel, A. Hagfeldt, *Nature Photonics* **2017**, *11*, 372–378.
- [4] E. Tanaka, H. Michaels, M. Freitag, N. Robertson, *Journal of Materials Chemistry A* **2020**, *8*, 1279–1287.
- [5] I. Mathews, P. J. King, F. Stafford, R. Frizzell, *IEEE Journal of Photovoltaics* **2016**, *6*, 230–235.
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GIF Young Investigator Awards 2021

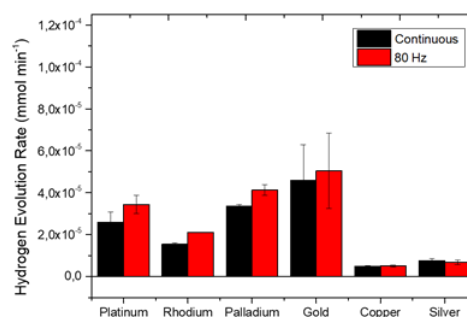
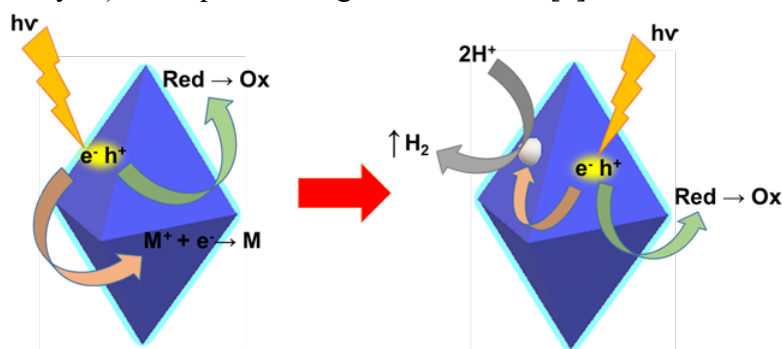
A New Strategy for Overcoming the Volcano in Water Photosplitting: Controlled Periodic Illumination

F. Pellegrino,^{a,b} F. Sordello,^a M. Prozzi,^a C. Minero,^a V. Maurino^{a,b}

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In the next decades, the conversion of solar energy into electricity and solar fuels will be of crucial importance for a green and sustainable future.[1] However, many challenges remain to exploit solar energy in an efficient way.[2] In this context, water splitting using semiconductor photo-catalysts has been considered a sustainable method to produce clean hydrogen (H₂) fuel.[3] Nevertheless, H₂ photo-production efficiency remains still low, although extensive research effort has been carried out in these years about the mechanisms of the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER).[4] In this respect, TiO₂ is a key photoactive material, usually employed with a co-catalyst deposited onto the surface to enhance charge carriers' separation and catalyze surface charge transfer reactions.[5] Even with a noble metal catalyst, the hydrogen evolution reaction can be limited by the strong M-H bonding over some metals, such as Pt, Pd and Rh, inhibiting hydrogen desorption. H absorption/desorption is regulated by the potential at the metal nanoparticles. Through controlled periodic illumination of metal/TiO₂ suspension, we hypothesized a fast variation of the photo-potential that result in more than 50% increase of the efficiency (only for specific co-catalysts) at frequencies higher than 80 Hz.[6]



- [1] A. Hauch et al., Recent advances in solid oxide cell technology for electrolysis. *Science* 370, (2020).
 [2] Z. W. Seh et al., Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* 355, (2017).
 [3] S. U. Khan et al., Efficient photochemical water splitting by a chemically modified n-TiO₂. *Science* 297, 2243-2245 (2002).
 [4] N. Armaroli, V. Balzani, The hydrogen issue. *ChemSusChem* 4, 21-36 (2011).
 [5] H. Zhang et al., Direct probing of atomically dispersed Ru species over multi-edged TiO₂ for highly efficient photocatalytic hydrogen evolution. *Sci Adv* 6, (2020).
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Premio "Ugo Mazzucato" per la miglior tesi di dottorato in fotochimica 2021

Silicon Nanocrystals Tailored for Bioimaging and Energy Conversion

Sara Angeloni^a

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My PhD thesis focus has been the development of hybrid organic-inorganic systems based on Silicon Nanocrystals (SiNCs) with possible applications in the field of bioimaging and solar energy conversion. SiNCs were engineered thanks to the realization of a strong covalent Si-C bond on their surface, which allowed us to disperse them in different solvents with different final purpose.

An organic-inorganic antenna system based on SiNCs conjugated with diphenylanthracene (DPA) photoactive molecules was realized and subsequently embedded into Luminescent Solar Concentrators (LSC) made of a polymeric matrix. [1,2] The optical and photovoltaic performances of this device were compared with the ones of a LSC embedded with a physical mixture made of SiNCs plus DPA at the same concentrations of the two components in the covalent system.

SiNCs were also functionalized with polyethylene glycol (PEG) chains in order to make them dispersible in water, for biomedical imaging applications. In vivo and ex vivo measurements were acquired in the Center for Imaging Medicine, Thayer School of Engineering, Dartmouth College. [3] The synthesis of dyes and/or SiNCs loaded Polymer Nanoparticles (PNPs) capable of excitation energy transfer (EET) mechanism is another theme I have explored during my PhD. This work has been started at the University of Strasbourg in the laboratory of Biophotonics and Pharmacology led by the professor Andrey Klymchenko.

Photo-switchable systems based on azobenzene derivatives-functionalized SiNCs were also synthesized. These organic-inorganic hybrid materials were studied to possibly obtain a new light-driven response of SiNCs. [4]

In the end I have been in America, at The University of Texas at Austin, in the laboratory led by the professor Brian Korgel. Here I have studied and compared the properties of high temperature hydrosilylated SiNCs and room temperature, radical promoted, hydrosilylated SiNCs.

This thesis work was financially supported by the University of Bologna and by the ERC proof of concept "Sinbiosys".

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Mean-field effects on the phosphorescence of dinuclear Re(I) complex polymorphs

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Collective and cooperative effects promoted by intermolecular interactions in condensed phases play a major role in the definition of the optical properties of molecular materials. The understanding of these phenomena is of great importance, as it allows to exploit supramolecular and crystal engineering to design and build materials with tailored responses. Interacting dyes are usually described invoking the so-called exciton approximation, which only accounts for interactions between the transition dipole moments of the interacting species [1]. Although this approach is accurate enough to rationalize the behaviour of nonpolar and hardly polarizable dyes upon aggregation, it can lead to failure when applied to polar and polarizable systems. Indeed, in the latter case, a significant charge redistribution occurs in response to the local electric field generated by the neighbouring molecules, introducing additional “mean-field” effects [2]. These self-consistent effects can have a strong spectroscopic impact, and survive even in the absence of exciton coupling, as in the case of phosphorescence. In this contribution, a computational (TD)DFT-based method describing mean-field effects was proposed and applied to two highly phosphorescent polymorphs of a dinuclear Re(I) complex, $\text{Re}_2(\mu\text{-Cl})_2(\text{CO})_6(\mu\text{-4,5-(Me}_3\text{Si)}_2\text{pyridazine})$ [3,4], rationalizing their different emission colours in qualitative and quantitative agreement with experimental data [5]. This study demonstrates that the proper description of mean-field effects is crucial for the rationalization of cooperative effects in polar/polarizable systems, and the effect of packing on phosphorescence can be exploited to tune the emission colour of materials (crystals, nanoparticles, films, multichromophoric assemblies) *via* supramolecular design.

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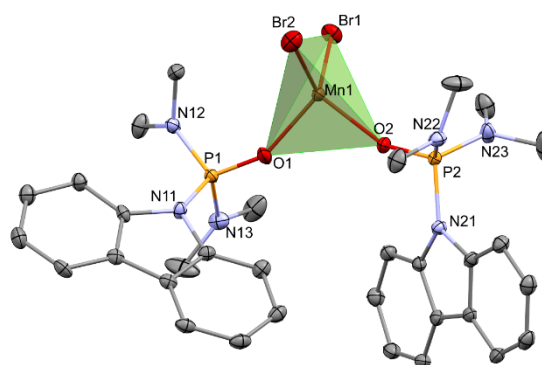
Green-emitting tetrahedral Mn(II) complexes with [O=P]-donor ligands

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Tetrahedral Mn(II) complexes are characterized by green luminescence related to the ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ transition.[1] These derivatives can be of potential interest for lighting applications, for instance as replacement of expensive rare earths-based phosphors in fluorescent lamps.[2] On the basis of recent outcomes on dihalide derivatives with phosphine oxides, phosphoramides, arylphosphonic diamides, amidophosphates and phosphonates were used as ligands L for the preparation of tetrahedral Mn(II) complexes having general formula $[MnX_2L_2]$ (X = Cl, Br, I).[3] 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 (SOC) effect. In the case of *N,N,N',N'*-tetramethyl-*P*-naphthalen-2-ylphosphonic diamide the first tetrahedral complexes exhibiting wavelength-dependent emission were isolated, characterized by two bands, one centred in the green and the other one in the red region of the spectrum. The latter is probably related to a ligand-centred tripled excited state (3LC), as further confirmed by computational calculations.[4] In most of the cases, the emission from Mn(II) is related, besides the direct excitation of the metal center, to the energy transfer from the excited states of the coordinated ligands. The absorption bands are essentially ascribable to the $\pi^* \leftarrow \pi$ transition of the aromatic moiety, as further confirmed by DFT calculations. The presence of a rigid structure and a light harvesting substituent such as the indolyl or the carbazolyl fragment in the skeleton of the [O=P]-donor ligands revealed to play a key aspect for the sensitization of Mn(II) luminescence.



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A monochromatic approximation for environmental photochemistry

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Photochemical reactions play a key role in the transformation of contaminants, and particularly of biorecalcitrant pollutants in sunlit surface waters [1]. The relevant processes, rates and overall importance can be predicted by photochemical modeling, based on sunlight irradiance and spectrum, water chemistry and depth, as well as pollutant photoreactivity (absorption spectrum, direct photolysis quantum yield and second-order reaction rate constants with photochemically produced reactive intermediates, PPRIs). Several pieces of evidence suggest that modeling is able to predict quite well the photochemical fate of several contaminants in surface waters [2].

A major issue that is connected with modeling is the polychromatic nature of sunlight, of the absorption spectra of contaminants and of the natural chromophores and photosensitizers (nitrate, nitrite and chromophoric dissolved organic matter, CDOM). Photosensitizers are the sources of PPRIs such as $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and CDOM triplet states, $^3\text{CDOM}^*$ [3]. In order to tackle polychromatic radiation, the monochromatic Lambert-Beer equation describing radiation absorption is to be applied for each relevant wavelength, and the results summed up together. Unavoidably, numerical integration is a fundamental prerequisite of photochemical models and it considerably complicates calculations, compared to the relatively simple Lambert-Beer equation. Therefore, photochemical modeling usually requires dedicated software [4] to be carried out. The latter, although often freely available, might not always be easy to customize.

This contribution shows how it is possible to overcome this difficulty by using monochromatic Lambert-Beer equations for photochemistry modeling instead of polychromatic, integral ones. The key to successful approximation is the definition of the equivalent monochromatic wavelength (EMW or λ_{eq}) [5]: it is the single wavelength which, when used in the Lambert-Beer equation that is monochromatic by nature, approximates the behavior of the polychromatic system.

Comparison between polychromatic and monochromatic, EMW-based equations was carried out and showed that nitrate photochemistry (source of $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$) can be described with EMW = 315 nm, nitrite photochemistry (producing the same PPRIs as nitrate) with EMW = 360 nm, and CDOM photochemistry (source of all PPRIs) with EMW = 560 nm. The EMW approach worked less well in the case of CDOM, because of the very broad overlap (a couple of hundreds nm) between CDOM absorption spectrum and the spectrum of sunlight. In this case a simple monochromatic equation struggles to summarize the behavior of polychromatic radiation in terms of water-column penetration and CDOM absorption. The solution was a modification of the Lambert-Beer equation by addition of an exponent that allowed the curvature to be changed with water depth, thereby emulating the behavior of the polychromatic system.

The EMW approach presented here allows for excellent agreement to be obtained between integral equations and monochromatic ones, with an error that is orders of magnitude lower than the inherent uncertainty of photochemistry models. It is thus possible to highly simplify calculations with virtually no loss in accuracy, and this advance paves up the way for extending photochemistry models to a global scale (some examples will be provided in this sense).

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The quest for triplet population and reducing ability in organic photoredox sensitizers: the case of BODIPY dyes

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Photoredox sensitizers are light-absorbing molecules that can trigger a sequence of photoinduced electron transfer events thanks to a long-lived excited state and appropriate redox potentials. Given these requirements, they have traditionally consisted in heavy metal complexes but considerations on their scarcity and toxicity has shifted the research towards the development of alternatives that don't contain such critical elements.

To this aim, we have investigated the derivatization of BODIPY dyes with the purpose of enabling efficient intersystem crossing and attaining more negative reduction potentials, which would allow them to take part in a wider variety of chemical transformations. Indeed, these chromophores possess a high molar absorption coefficient and good photostability, and strategies to allow them to populate their triplet excited state have been recently developed[1]. We therefore synthesized derivatives belonging to two classes, iodinated ones and donor-acceptor dyads. The newly synthesized derivatives were characterized photophysically, so as to study the accessibility of their triplet excited state, and electrochemically, so as to investigate their reduction process. Finally, we studied their behavior under irradiation in the presence of a sacrificial electron donor to further explore their ability to perform as photosensitizers for CO₂ reduction and photoredox catalysis.

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Ketene 3-Component Staudinger Reaction (K-3CSR): a novel photoinduced approach to the synthesis of β -Lactams

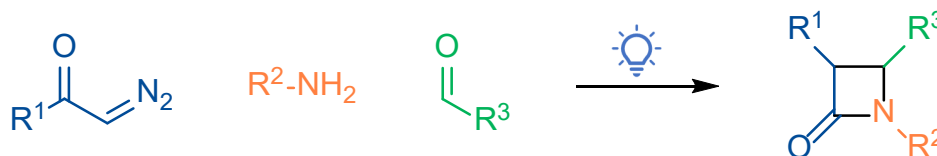
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The Staudinger synthesis of β -lactams was performed, for the first time, as a photoinduced three component reaction.[1]

The photoinduced Staudinger reaction has already been reported in literature as a bicomponent approach between preformed imines and diazoketones. In this case highly energetic UV irradiation was used to favour the Wolff Rearrangement of diazoketones to ketenes.[2]

The novel methodology reported in this contribution uses visible-light instead,[3] and both ketenes and imines are generated *in situ* and directly employed in the Staudinger [2+2] cycloaddition. Synthetic simplicity, high efficiency and complete stereoselectivity are some features of the Ketene 3-Component Staudinger Reaction (K-3CSR). Due to the intrinsic reactivity of ketenes and amines, the key to the success of the process was performing the reaction in the dark and switching the light on only upon imine formation. An optimization of the reaction conditions was performed, and the outcome was compared with that of the *classic* two component reaction. Moreover, the quantum yield of the visible-light mediated Wolff Rearrangement was calculated and found to be close to 100%. Finally, a library of compounds was realized exploiting this new methodology.



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Photocatalyzed functionalization of α,β -unsaturated carboxylic acids

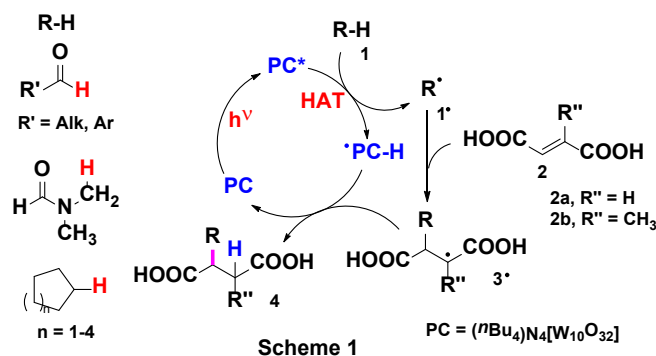
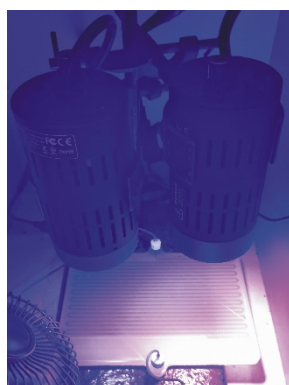
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The selective functionalization of α,β -unsaturated carboxylic acids with nucleophilic reaction partners is not an easy task because of the presence of acidic hydrogens, possibly leading to mixtures of products. In this project, we explored the functionalization of these acids under radical-mediated photocatalyzed processes, complementing our recent work on the derivatization of crotonic acid. [1] Our group is deeply involved in the development of photocatalytic methods for the photogeneration of C-centered radicals and the ensuing addition onto electron-poor olefins. [2] This strategy is based on the use of tetrabutylammonium decatungstate (TBADT, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$) as the photocatalyst. [3] Upon absorption of a photon, this compound is able to cleave homolytically (often with high chemo- and regioselectivity) C–H bonds in a variety of organic derivatives through a Hydrogen Atom Transfer (HAT) step. [4] Accordingly, we achieved the smooth $\text{C}(\text{sp}^3)\text{--H}$ functionalization of aldehydes, amides and alkanes (see R–H **1** in Scheme 1 below). [3,4]



In this work we applied this approach to two α,β -unsaturated dicarboxylic acids with different steric hindrance on the double bond, namely fumaric (**2a**) and citraconic (**2b**) acids (Scheme 1). Thus, the photogenerated radical

1* was trapped by **2** to give radical adduct **3***, in turn involved in the regeneration of the photocatalyst (via a back-HAT step) and leading to the desired product **4**. In the case of **2b** functionalization, the selectivity in the addition step onto the two non-equivalent positions of the double bond has been likewise evaluated, showing a dependency on the nature of the photogenerated radical. Notably, these reactions could be easily adapted to flow conditions, by adopting a home-made reactor or a 3D printed microreactor made of polypropylene (PP; see picture on the left in Scheme 1).

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Multi-photoactive BAPO-cyclodextrin: a *two-in-one* photoinitiator and photocrosslinking agent

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A novel multifunctional photoinitiator (MFPI) was successfully prepared decorating natural γ -cyclodextrins (γ -CyD) with photoactive bis(acyl)phosphane oxide (BAPO) units.

The multiple hydroxyl sites of γ -CyD were first substituted with acrylate functions which then serve as activated olefinic substrate for the Phospha-Michael addition of a BAPO precursor, yielding the multi-photoactive BAPO- γ -CyD as molecularly well-defined MFPI.[1] The success of the convergent synthesis was confirmed by ¹H-, ¹³C-, ³¹P-NMR and IR spectroscopy and mass spectrometry.

Kinetic studies carried out by photo-differential scanning calorimetry and photo-rheology proved the outstanding efficiency of BAPO- γ -CyD as multiple photoinitiator for free radical polymerization, even when using it at very low molar concentrations. This might be of high interest for those applications wherein a high-molecular weight photoinitiator must be used to guarantee low migration without any loss of photoactivity.

Remarkably, this novel MFPI stand out over the conventional molecular photoinitiators by serving simultaneously as photocrosslinking agent to convert monofunctional monomers into mechanically stable thermosets. This unique feature was successfully exploited to get photocured polymers with extensive swelling capability in water starting from monofunctional methacrylates, and mostly to develop innovative “crosslinkers-free” formulations for the preparation of shape memory polymers via digital light processing (DLP) 3D-printing.[2]

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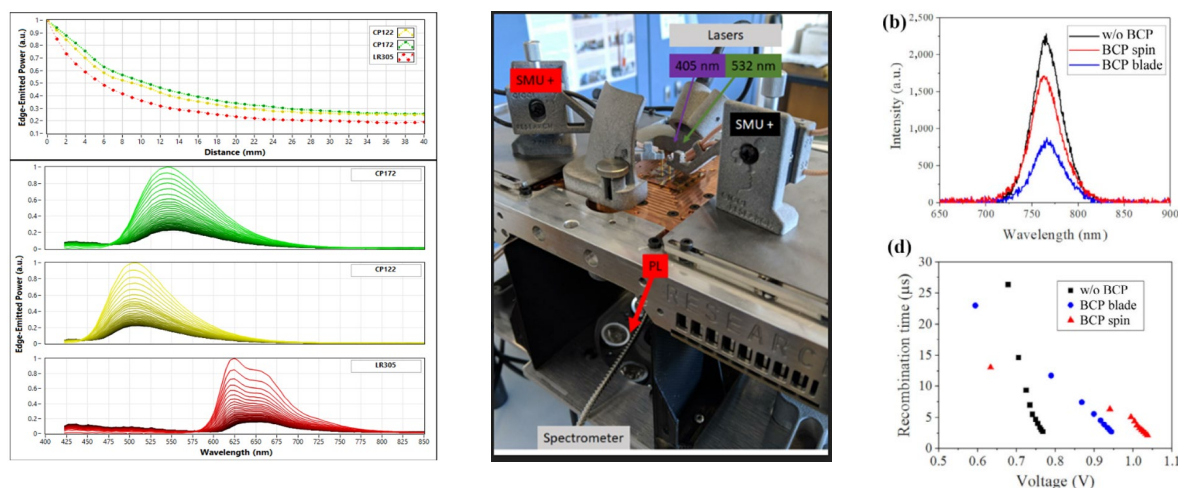
Charge recombination dynamics: an experimental approach from perovskite-based devices to luminescent solar concentrators

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Steady-state and dynamic electro-optical tests on hybrid organic-inorganic photovoltaic (PV) devices, when properly performed, can give advanced knowledge on physical parameters like charge carrier diffusion length or recombination times at the active layer/selective contact interface. The goal is to correlate information from steady-state and small-high perturbation dynamic tests (TPV, charge extraction, EIS, etc.). We developed a reliable analysis to investigate charge carrier recombination dynamics by quantifying internal-external quantum efficiency, recombination dynamics and radiative emission. Case studies on luminescent solar concentrators (LSC) and blade-coated perovskite solar cells (SC) will be presented.



Left: photo-luminescence spatial decay on LSC; **Middle:** Arkeo experimental setup; **Right:** electro-luminescence and charge lifetime of perovskite SC.

Acknowledgements: This work was funded by COLOURS (POR-FESR Tuscany Region).

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Photopolymerization of hyperbranched networks by thiol-ene “click” reaction in cobalt-based electrolytes for Dye-Sensitized Solar Cells

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We studied the performance of Dye-Sensitized Solar Cells employing cobalt-based electrolytes with hyperbranched networks HB1 (thiol-siloxane and PEGMA) and HB2 (thiol-siloxane and PEGMA) formed by the photo-induced thiol-ene “click” reaction shown in Fig 1. By FTIR monitoring, we found that 1 min of UV-curation was sufficient to complete the reactions. TGA analysis showed that electrolytes containing 20% of HB1 and HB2 retained 98% of their initial weight up to 150 °C.

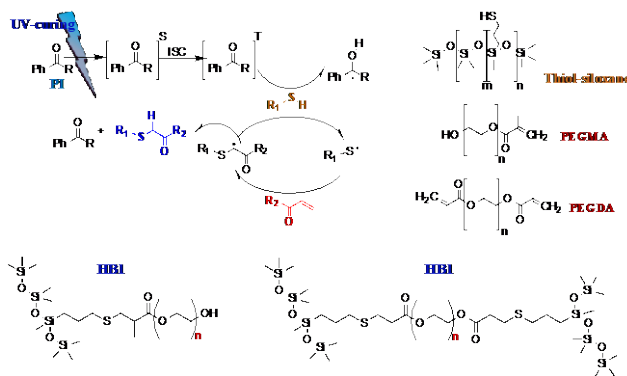


Figure 1. Thiol-ene reaction and molecular structures of thiol-siloxane, polyacrylate monomers PEGMA, and PEGDA and simplified hyperbranched products, HB1 (PEGMA+thiolsiloxane) and HB2 (PEGDA+thiolsiloxane).

Devices with 10% (w/w) of HB1 in the cobalt electrolyte reached an open circuit voltage (V_{OC}) of 875 mV, short circuit current (J_{SC}) of 14.75 mAcm⁻², and fill factor FF of 0.66 for a power conversion efficiency (PCE) of 8.52% under 1 sun illumination, comparable to a PCE of 9.36% for the cobalt reference. For higher polymeric contents, low PCEs under 1 sun result from low diffusion coefficients for Co³⁺ in the electrolytes. All devices with HB electrolytes presented higher V_{OC} values due to an upward-shift of the TiO₂ CB and longer electron lifetimes than the Co^{3+/2+} as disclosed by EIS analysis under 1 sun illumination. EIS analysis also revealed that the higher performance for all the devices with HB1 and HB2 under low light intensity is attributed to higher R_{CT} and lower R_{trans} , leading to a PCE of 23.19% under 1000 lux for devices containing 15% of HB1 compared to 20.37% for the Co-reference.

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Metal-based photosensitizers and catalysts for light-to-energy conversion

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In the twenty-first century, the humankind still depends on non-renewable energy source. Exploiting fossil resources causes a large quantity of emissions and, as consequence, climate changes, e.g. global warming, and several pollution. On the other side, in all this centuries, the nature has taken advantage of solar light to satisfy its energetic demand, via natural photosynthesis without side effects.[1] Indeed, solar energy is the most abundant, inexhaustive and renewable energy source. The goal of the research on these topics, in the last decades, was mimic natural photosynthetic systems to obtain artificial photosynthetic systems which can convert the solar light in useful chemicals like hydrogen, formic acid, oxygen or carbon monoxide (see **Figure 1**).[2] Nevertheless, the natural systems are too complex and so they can be only functionally reproduced. To this aim, we synthesized, characterized, and studied multicomponent systems made of metal complexes as photosensitizer, to harvest solar light, and as suitable catalysts able to convert water or CO₂ in useful energy rich chemicals.[3,4]

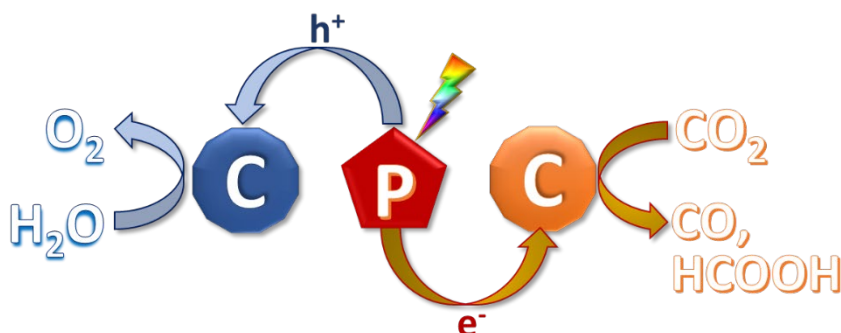


Figure 1. Scheme of artificial photosynthetic systems.

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A Series of Iron(II)-NHC Sensitizers with Remarkable Power Conversion Efficiency in Photoelectrochemical Cells

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Dye Sensitizer Solar Cells (DSSCs) are characterized by unique features such as transparency, low fabrication cost, capability to harvest the diffuse light as well as the availability of a wide palette of color. These peculiarities make them interesting photovoltaic devices for indoor and architectonic applications.[1] Substituted polypyridine Ruthenium complexes have been long regarded as the top sensitizers for their broad light absorption and for their tunable photophysical and redox properties leading to an overall cell efficiency ranging to 11-14%.[2] The scarcity and toxicity of this metal have been moving the attention to the first-row elements such as iron, cobalt and zinc. Since the pioneering contribution of Ferrere and Gregg, Fe(II) complexes revealed the possibility to give photocurrent when anchored to a semiconductor substrate despite the less of 0.1% efficiency due to the fast deactivation of the ^{1,3}MLCT states to an MC level. Our group has firstly obtained 1% cell efficiency with a homoleptic iron Carbene (NHC)-based sensitizer namely **C1**,[3] overcome by its heteroleptic analog **ARM13**, reaching a 1.5% power conversion efficiency (PCE).[4] We further synthesized and characterized another series of six heteroleptic Fe(II)NHC complexes characterized by the introduction of electron withdrawing or donating moieties on the ancillary ligands. To address the heterogeneous charge transfer dynamics, we employed electrochemical, photoelectrochemical and photophysical experiments as well as computational calculations. **ARM130** characterized by dimethoxyphenyl group on one of the pyridines, gave the best combination of photocurrent density (J_{SC}) of 6.80 ± 0.17 mA/cm² and open circuit photovoltage (V_{OC}) (0.47 ± 0.02 V) thanks to the broad and intense absorption ranging from 400 to 600 nm, a favorable excited CT directionality and slow recombination kinetics. With **ARM 130**, by exploiting an optimized electrolyte and TiO₂ photoanode, we have obtained 2% efficiency, which is, to the best of our knowledge, the highest efficiency ever recorded for a Fe-sensitized DSSC

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Interaction of a TiO₂ Surface with Organophosphonic Acids: the Role of pH

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We propose a computational model, using DFT and DFTB theory, to investigate the grafting of a rutile titanium dioxide (TiO₂) surface to dodecyl-phosphonic acid (C12-PA). The resulting organic–inorganic hybrid material allows to specifically tune the surface properties combining the structural, chemical and mechanical characteristics of metal oxides with the great versatility of organic molecules [1]. The material can be used in different photochemical applications [2] and as an anchoring system for photo-catalysts [3].

The TiO₂ surface, besides being low-cost, proved to be important in many fields such as photoelectrochemistry [4]. On the other hand, C12-PA, and more generally organophosphonic acids (OPAs), are widely used for grafting these metal oxides [5]. The phosphonate groups of OPAs are able to bind the surface in a mono- bi- and tri-dentate way, as experimentally reported [5]. These interactions were also studied in several theoretical works, but only neutral OPAs were taken into account and the formation of tri-dentate species have not been reported [6].

This contribution aims to elucidate the nature of the interactions between the (110) TiO₂ rutile surface and C12-PA as a function of pH, by studying the three forms of C12-PA: neutral, anionic and di-anionic. Furthermore, we propose a reaction pathway, which includes proton transfers between the acid and the surface, for the formation of the tri-coordinate C12-PA species.

All calculations were carried out with the DFTB plus software, using the MATSCI parameters. The results are validated with the use of the ORCA and Quantum Espresso software. The reaction pathway between TiO₂ and C12-PA was divided in three different steps. In the first step, the neutral and anionic species anchor the surface with a bi-dentate coordination: accordingly, the anionic C12-PA affords more stable interactions (lower ΔE values) with the surface than neutral one. In the second step, both species can transfer one (for anionic) or two (for neutral) protons to the surface. These proton transfers (PT) stabilize the interaction between the acid and the surface, so that the investigated systems tend to reach the same energies for both species (neutral and anionic). In the third step, both C12-PA species were able to form a third bond with the surface; however, these structures are destabilized in energy. Consequently, the tri-dentate species could be formed only in small amounts as found experimentally [5]. Also the di-anionic species prefers to coordinate to the surface in a bi-dentate way and, as observed for the previous cases, the tri-coordinate species is destabilized in energy. However, this species is characterized by lower ΔE values, resulting in the strongest interaction between C12-PA and the TiO₂ surface.

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Utilizing upconversion via triplet-triplet annihilation for radiation modulation and optical communication experiments

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Upconversion based on triplet-triplet annihilation (TTA-UC) is a phenomenon involving light-matter interactions, in which two low-energy photons are converted in one photon with higher-energy.[1] This intriguing mechanism has attracted significant attention from the scientific community in the last decades, due to the wide range of fields in which TTA-UC can be applied.[2,3]

We present the application of UC solution, composed by a benchmark couple, platinum octa-ethylporphyrin (PtOEP) and 9,10-diphenylanthracene DPA (chosen as sensitizer and emitter, respectively) in oleic acid, for optical communications [4] with n-octylacridinium perchlorate ($\text{Acr}^+\text{ClO}_4^-$). The experiment provides the excitation of the sensitizer with green light, that undergoes an efficient ISC to populate its triplet state ($^3\text{T}^*$); then, triplet-triplet energy transfer (TTET) allows the $^3\text{T}^*$ population of DPA. Upon TTA between emitter excited states, blue fluorescence is observable. The UC solution transmits the blue emission to the receiver $\text{Acr}^+\text{ClO}_4^-$; whose emission spectrum overlaps with the absorption transitions of PtOEP. The results show that even in absence of physical contact between transmitter and receiver, interactions occur and they have a purely optical nature.

We also prepare solid-like materials [5] able to generate the green-to-blue upconverted signal in air-equilibrated conditions, exciting with an incoherent light source. Oil-core/silica shell nanocapsules (UC-NC) have been synthesized and fully characterized with spectroscopic and microscopic techniques. The core phase consists of oleic acid containing the upconverting molecular pair (PtOEP/DPA); the silica shell is grown to have a 10-15 nm thickness in order to act as a protective barrier and compartmentalize the pair.[6,7]

The synthesized UC-NC attest their solidness even in severe conditions, such as those of the Belousov-Zhabotinsky (BZ) periodic reaction.[8] In fact, UC-NC have been employed for the modulation of UV periodic radiation transmitted by the BZ reaction, in the visible range, in order to develop a system similar to a demultiplexer. The results demonstrate that the rigid silica shell of the nanocapsules is efficient in protecting the luminescent nanostructured materials broadening the optical output of the sample.

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Direct NAD(P)H regeneration using light: a novel application of an old compound

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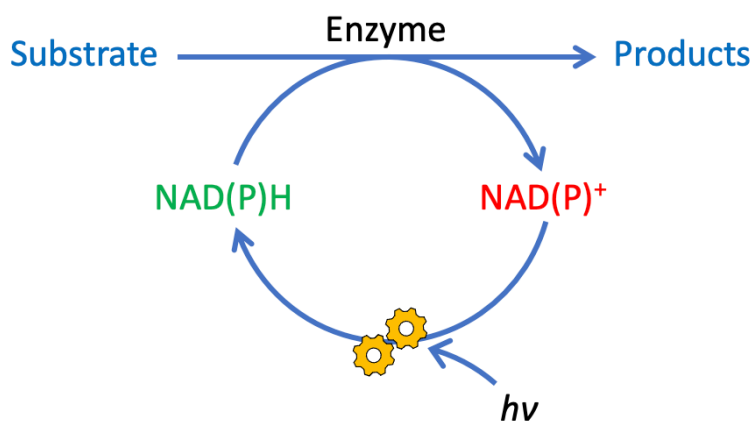
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Enzyme catalysis is a highly active, selective, specific and sustainable process for high-value chemicals' production, but it generally requires one or more cofactors which are consumed during the reaction.[1–4] This latter aspect, combined with cofactors' high cost, represents the main limitation to a practical applications of this approach, so an effective system for cofactor regeneration would be a significant step forward.[2,5]

A quarter of all enzymes is represented by oxidoreductase, a type of enzyme which mainly depend on Nicotinamide Adenine Dinucleotide (NAD⁺) or its phosphate (NADP⁺); so many approaches for NAD(P)⁺ reduction have been investigated;[2,5–7] among all proposed methods, photochemical NAD(P)H regeneration is the most attractive, because sunlight is clean, inexpensive and abundant.[2,5]

In this scenario we developed a system for NAD(P)H regeneration based on a scarcely known ruthenium complex, [Ru(bpy)CN₄]²⁻, which is a very good photo-reductant (E_{P+*/P} = -1.6 V vs SCE in water)[8], and a sacrificial electron donor, such as TEOA or L-Cysteine.

That system has proved to be very photostable, giving high-conversion rates of NAD(P)⁺ in short time and, to date, it represents one of the very few systems which performs direct reduction without any mediator.[2]



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A Doxorubicin-NO Releaser Molecular Hybrid Activatable by Green Light to Overcome Resistance in Breast Cancer Cells

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Doxorubicin (DOX) is one of the most used anti-cancer drugs for treatment of a large variety of tumors. However, its use is hindered by the dose-dependent cardiotoxicity and the development of multidrug resistance (MDR). Different mechanisms are at the basis of MDR; the resistance to DOX is mainly exerted through its increased efflux from cancer cells as result of the overexpression of adenosine 5'-triphosphate (ATP) binding cassette (ABC) transporters. Many strategies have been proposed to overcome MDR, in particular coadministration of DOX with compounds able to inhibit the activity of ABC transporters [1]. Nitric Oxide (NO) is the ideal candidate for this purpose since it is able to nitrate critical tyrosine residues of the transporters [2]. As the dose of NO is crucial to reach the desired biological effect, an accurate control of its delivery is mandatory. Light represents a powerful tool to fulfil this need with high spatiotemporal control by using appropriate photoprecursors namely NO Photodons (NOPDs) [3]. We report for the first time a NOPD operated by DOX as light-harvesting antenna. It permits NO uncaging from a N-nitroso appendage upon selective excitation of DOX with the highly biocompatible green light, without precluding its typical red emission useful for the localization of the hybrid within the cellular environment [1,4]. The photochemical characterization and the biological activity will be discussed.

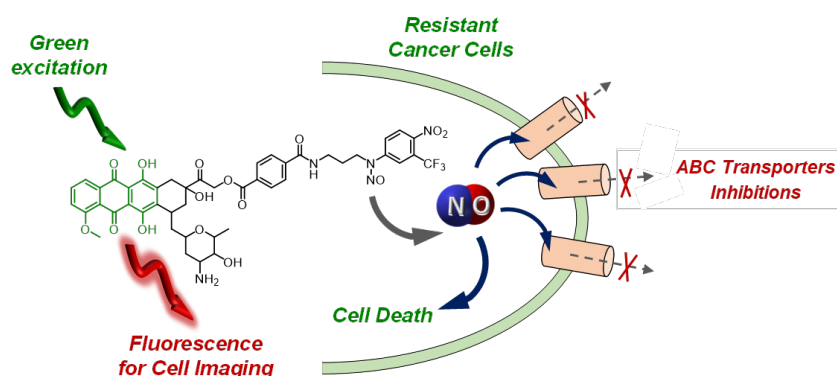


Figure 1. Structure of the hybrid releasing NO under green light excitation and its main activity.

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An Insight into the Excited-State Deactivation Mechanism of new Aggregation-Induced Emission Materials for Biological Applications and Optoelectronics

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The continuous investigation of luminescent materials has made possible to design and manipulate these systems at the molecular level allowing to use them in many fields of application. The investigations in solution have made a great contribution to the fundamental understanding of the processes involving the emission of light. The conclusions drawn from the data collected in diluted solution, however, cannot be extended generically to concentrated or aqueous solutions and solid state. In fact, many organic luminophores tend to show a drastic decrease of the fluorescence yield when passing from dilute to very concentrated solutions. This is caused by the Aggregation-Caused Quenching (ACQ) effect. This problem is very serious because it limits the applicability of fluorophores both in biological environment and in the manufacture of optoelectronic devices. In 2001, Tang et al.[1] have discovered and renamed the phenomenon of Aggregation-Induced Emission (AIE) that offers a straightforward remedy to all these issues.

In this light, the aim of our research was the investigation of three different families of push-pull compounds showing AIE properties. We have selected several sets of compounds as each of them allows us to probe different phenomena around the main one of the formation of aggregates. Altogether, in fact, it was possible to deepen our understanding of the impact of the molecular structure on the AIE effect and to highlight interesting photo-physical behaviors exploitable for the design of Room Temperature Phosphorescence (RTP) materials and fluorescent probes for biological sensing and Photodynamic Therapy (PDT). [2-5]

Specifically, in this work, these compounds were investigated in a wide set of organic solvents, in water dispersion and in solid state to evaluate the impact of the medium on the emission phenomena and on the processes that compete with the radiative deactivation, such as intramolecular charge transfer (ICT) and inter system crossing (ISC). This study was carried out by means of steady-state and time-resolved absorption, fluorescence and phosphorescence spectroscopy. In particular, advanced spectroscopic techniques, such as nanosecond and femtosecond transient absorption and femtosecond broadband fluorescence up-conversion as well as non-linear two photon excited fluorescence, were employed to follow the dynamics of the lowest excited singlet and triplet states.

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Tunable Near-Infrared Emitting Nanoclusters: an in-situ spectroelectrochemical fluorescence study

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Monolayer-protected metal clusters, MPCs with a metallic (Au, Ag, etc.) core of less than 2 nm and tailored capping monolayer, are emerging as atomically precise candidates to gain sought opto-electronic properties to be exploited in catalytic, energy conversion and nanomedicine applications.[1][2] However, while the electronic and structural properties of most MPCs are nowadays well understood, the origin of the peculiar near-infrared photoluminescence (PL) properties of these ultras small MPCs remains an open question:[3] intraband and interband transitions, surface or 'semi-ring' states, or ligand-metal charge transfer states have been indeed alternately assigned to justify the mechanism of the MPCs emission. [4]

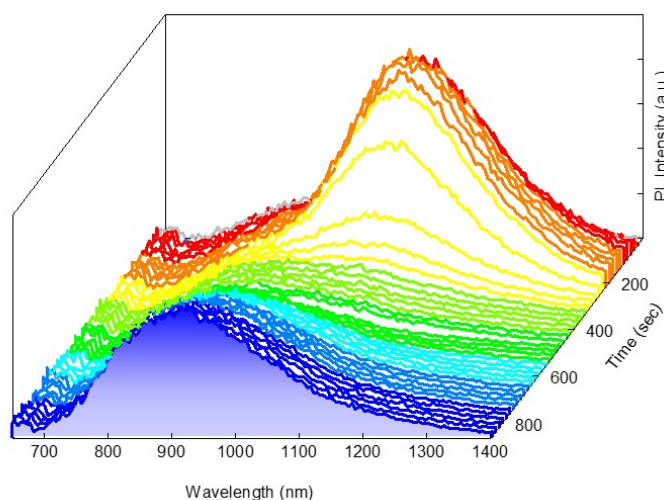


Figure 1. Spooling spectroelectrochemical Fluorescence of Monolayer-protected metal clusters.

In this framework, we describe *in situ* absorption and photoluminescence spectroelectrochemical analysis of gold [Au₂₅(SPh)₁₈] as straightforward method to shed light on the dependence of the optical properties of the MPCs on their electronic charges [i.e. (+1), (0), (-1)], thereby giving an important contribution to resolve the physical origins of the NCs emission. Moreover, highly tunable stock-shift in the near-infrared region can be achieved by means of an electrochemical input. [5]

Our experimental results, also supported by X-Ray analysis and theoretical investigation of NCs electron and nuclear dynamic, highlight how the coupling of the electrochemical and optical investigations is

essential to fully exploit the unique properties of the MPCs and to design novel structures with enhanced optical properties.

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3-Oxidopicolinate: A surprising short bridge for generating bright phosphorescence from binuclear iridium(III) complexes

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The development of transition-metal complexes for optoelectronic applications is still a fertile research field. Apart from the conventional development of mononuclear complexes, binuclear species have been less investigated, mostly due to more complicated routes for their synthesis and characterization; as a consequence, their fundamental chemistry may still present unexpected properties and their related applications are virtually unexplored.[1]

Herein, we serendipitously found 3-oxidopicolinate to simultaneously coordinate two cyclometalated iridium(III) centers, when adequate synthetic conditions are provided. To impart more versatility, we employed both identical and non-identical cyclometalating ligands on either side of the bridge. It must be emphasized that asymmetrical binuclear cyclometalated iridium(III) complexes are not known yet, probably due to synthetic difficulties. The photophysical properties of these newly developed binuclear complexes are judiciously tuned taking advantage of the different nature of the coordinating ligands.

This short talk will unravel the exciting path towards the synthesis of this new class of iridium(III) compounds, how the combinatorial approach from experimental and theoretical knowledge leads us to distinguish the two couples racemic enantiomers (*i.e.*, the $\Delta\Delta'$ and $\Lambda\Lambda'$ couple *vs.* the $\Delta\Delta'$ and $\Lambda\Lambda'$ counterpart) and finally their associated photophysical properties.

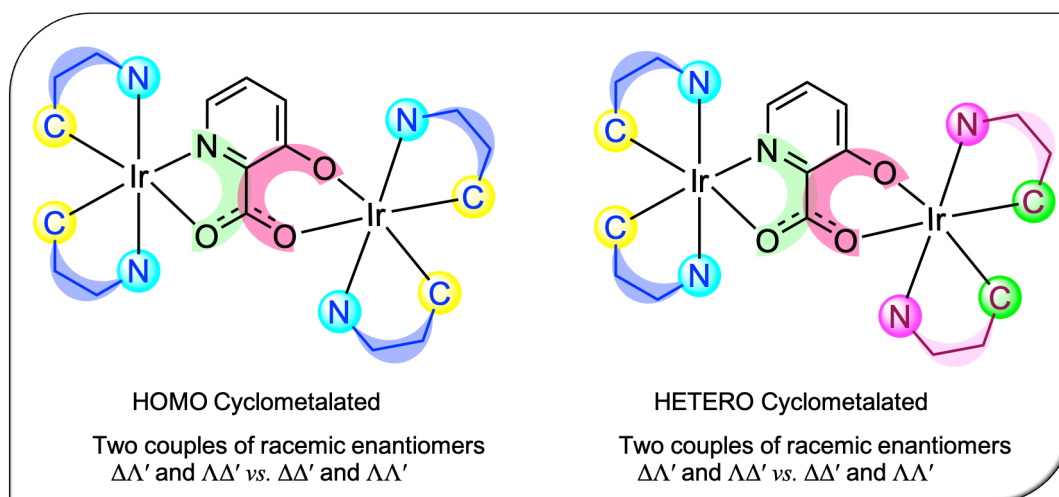


Figure 1. Schematic of new picolinate bridged binuclear iridium(III) complexes.

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Local Light-controlled Generation of Calcium Carbonate and Barium Carbonate Biomorphs via Photochemical Stimulation.

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Photochemical processes for the production of solid materials from liquid precursors are at the basis of the most advanced technologies for micro- and nano-fabrication because light activation allows to have a high control in space and time [1]. In this field, photoreactions have been mostly used to produce organic polymeric materials [2], rather than inorganic materials, which are, however, scientifically and technologically important.

Here we demonstrate, for the first time, that photo-activation can be used as a general method to control the crystallization of sparingly soluble carbonates in space and time. Our “photo-precipitation” technique is based on the use of Ketoprofen as a photo-CO₂ generator, that, once irradiated, promotes the precipitation of alkaline-earth carbonates. In this work, this principle has been widely studied with the aim of “writing” CaCO₃ structures on a surface by the irradiation of an aqueous solution in presence of Ketoprofen and Ca²⁺ ions. CaCO₃ crystals formation was locally obtained on a glass surface, but also in a transparent gel, fixing CaCO₃ structures in a matrix. The same mechanism was also exploited to precipitate BaCO₃, promoting the formation of BaCO₃/SiO₂ biomorphs, and can be, in principle, applied to many photo-labile molecules to obtain controlled precipitation of other inorganic materials.

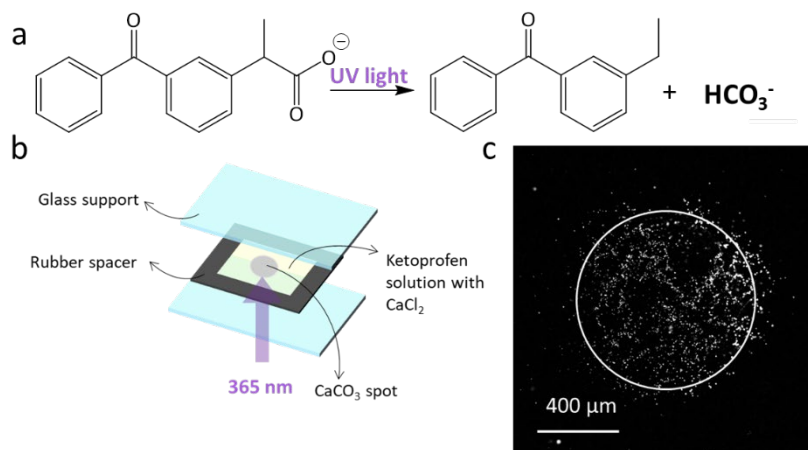


Figure 1: a) Ketoprofen photodecarboxylation reaction, which, in alkaline environment, produces carbonate ions; b) setup used for the photo-precipitation of CaCO₃. The Ketoprofen and CaCl₂ solution is placed between two glass supports and irradiated with a focused LED (365 nm); c) spot of CaCO₃ crystals obtained after irradiation, selectively in the irradiated area, observed in an optical microscope [3].

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Supramolecular-based fluorescent ligands as sensing tools for the detection of emerging pollutants

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Emerging pollutants (EPs) cover different families of natural or anthropogenic substances, such as pesticides, antibiotics, anti-inflammatory drugs, personal care products, plastics, mostly derived from industrial wastewater, domestic effluents or agriculture waste.

The great concern about emerging pollutants arises from their proven hazardous effects on environmental, human and wildlife health.[1] Despite sensitive techniques to detect contaminants in waters are already used, they suffer from the major drawbacks of requiring long-time sample preparation and qualified personnel. To fulfil the increasing interest in tracking of pollutants in real-time, a promising strategy is the design of optical sensors based on luminescent chemosensors [2], that are able to ensure a fast, cost-effective real time analysis of samples.

Here we report a complete photophysical characterization of a family of supramolecular fluorescent probes and the study of their interaction with ketoprofen and naproxen, that belongs to the important class of EPs represented by nonsteroidal anti-inflammatory drugs (NSAIDs).

These macrocyclic or pseudomacrocyclic probes have the dansyl as signalling unit and squaramides moieties supplying both strong hydrogen bond donor groups and an overall rigidity to the structure; they have been purposely designed to have multiple binding sites for the different targets, to improve the affinity and selectivity towards the target analytes, and reducing the interactions with interferents, such as inorganic anions, usually found in real matrices.

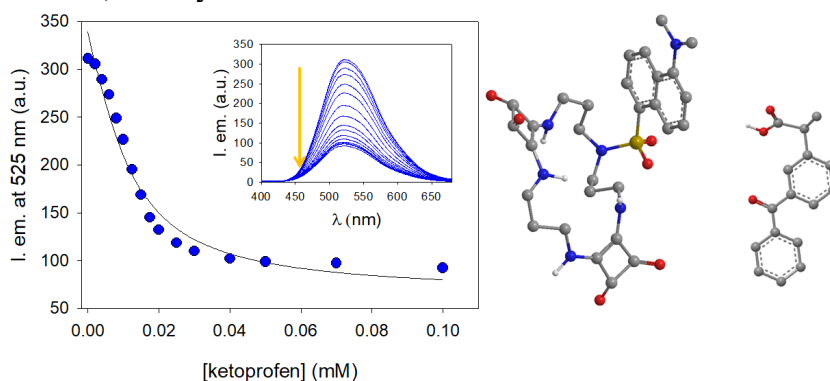


Figure 2: trend of emission at maxima versus concentration of ketoprofen of one of the investigated probe (left) and emission spectra upon addition of increasing amount of ketoprofen (inset); 3D structures of the probe and ketoprofen (right).

All of these probes successfully complex ketoprofen in acetonitrile with high association constants via H-bonds and hydrophobic interactions, at micromolar concentrations, resulting in a loss of luminescence signal and a shortening of their lifetime.

In addition, the stoichiometry of the adducts have been investigated in solution and competition studies were performed, assessing their specificity toward analytes and their overall selectivity.

This work is thus a promising step toward the design of arrays of chemosensors for efficient and sensitive detection of NSAIDs.

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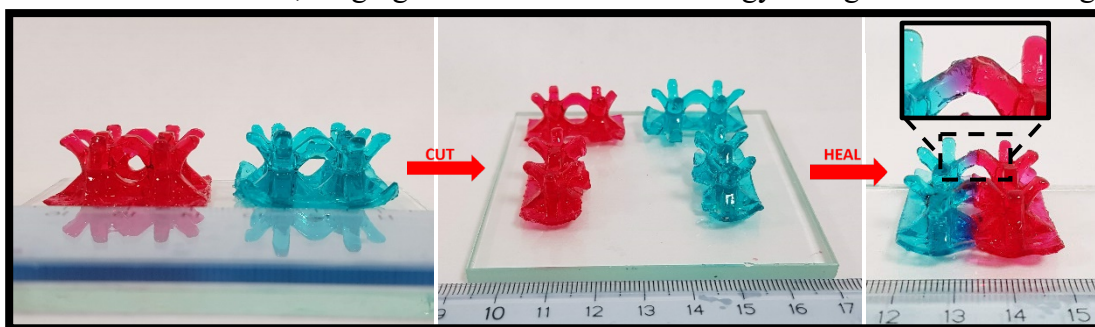
PVA-based DLP- 3D printed self-healing hydrogels

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The shaping of soft materials, such as hydrogels, into freeform self-supporting complex architectures is challenging unless it is performed through additive manufacturing (AM) fabrication. However, the mechanical properties required to bear their own weight can be achieved only if the polymer network has a high crosslinking density. This feature is typical of objects fabricated using light-activated 3D printing, in particular Vat photopolymerization (VP), which enables the accurate tuning of the structure while preserving freedom of design and resolution. The downside of the mechanical stability is a limitation in the lifetime because of irreversible failures. The addition of self-healing (SH) ability could push water-containing soft materials beyond their regular applications in biomedicine because they would be able to replicate sophisticated natural architectures thanks to 3D printing and at the same time mimic the behavior of living tissues, which can autonomously repair minor damage. In particular, intrinsic SH relies on specific functional groups embedded along the polymer chain that can interact across the severed interface, establishing new bonding without requiring the introduction of an adhesive [1]. Designing interpenetrated network (IPN) hydrogels enables to combine VP printability and SH, based on opposite requirements due to the dependence of the latter on chain migration and labile bonds, strongly hindered in a dense and rigid network [2].

We successfully overcome the apparent incompatibility between the VP printing process and the self-repairing properties by merging their intriguing characteristics into a semi-IPN which combined non-reversible bonds, provided by chemically cross-linked acrylic acid (AAc) and Poly (ethylene glycol) diacrylate (PEGDA), with reversible interactions established by uncrosslinked Poly (vinyl alcohol) (PVA) [3]. The covalent network was built using a commercially available Digital Light Processing (DLP) printer using a waterborne formulation containing a PVA solution, photocurable materials, and a water-soluble photoinitiator. A modification of the printer to flux aerosol in the vat was required to successfully fabricate structures comprising overhanging and hollow features. These showed rapid and autonomous self-healing at room temperature with no external stimuli, owing to the physical network established by PVA via strong hydrogen bonding. The samples could withstand bending and stretching deformation after restoration without failure, and the restoration efficiency was characterized by performing tensile tests on dumbbell-shaped samples, resulting in a 72% recovery of their pristine tensile strength after healing for 12 hours. The proposed approach offers a versatile start to develop self-repairing hydrogels with complex 3D architecture, paving the way for future applications in diverse fields, ranging from soft robotics to energy storage and artificial organs.



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Photochemical route to CDs-Au nanohybrid for photothermal applications

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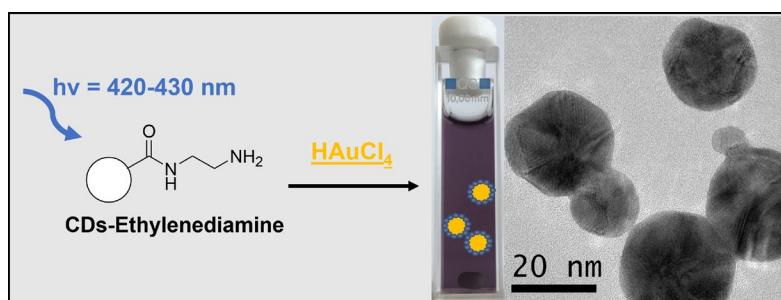
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Over the years, the study and preparation of gold nanoparticles (GNPs) have increasingly attracted the interest of researchers due to their excellent physical and chemical properties. In general, the possibility of appropriate surface functionalization makes them biocompatible and addressable, and they exhibit specific size- and shape-dependent optical and electronic properties [1]. Together, these excellent properties of GNPs demonstrate their enormous potential for use in various biomedical applications, including, for example, photothermal therapy. Carbon dots (CDs) are quasi-spherical carbonaceous nanoparticles, generally less than 10 nm, with sp²-sp³ core and an irregular surface rich of polar groups that confers aqueous dispersibility, easy post-functionalization, intriguing photophysical properties [2] and great biocompatibility [3].

Here we report, a one-step route for a visible-light triggered CDs-Au nanohybrid preparation using CDs as both reducing and capping agent. Precursors CDs were prepared from olive solid wastes [4] and functionalized with ethylenediamine via amide bond formation. Actually, amine and amide groups are known for Au(III) complexing ability [5] and amine to bind AuNPs surface [6]. CDs excited states, generated by blue light irradiation, served both as electron donors, for Au(III) reduction to Au(0), and acceptors for the counterpart. The new CDs-Au system was fully characterized via UV/Vis, fluorescence, FT-IR, EDX spectroscopies and SEM and TEM imaging. Its photothermal ability was also evaluated showing, with promising preliminary results, comparable light-to-heat energy conversion efficiency to the "gold standard" citrate-capped AuNPs by Turkevich.



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Biofriendly Route to Gold Nanoplasmonics through Mixed Cyclodextrin Branched Polymers Photoreleasing Nitric Oxide

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Over the past few years, gold nanoparticles (AuNPs) have been considered extremely desirable agents in the field of nanomedicine for their fascinating optical properties, owing to their surface plasmon resonance (LSPR) falling in the near infrared region (NIR) [1]. For this reason, these metal nanostructures are photoactivable in the so-called “therapeutic window” ($\lambda_{exc} = 650\text{--}1300\text{ nm}$) and rapidly convert light stimuli into heat with fine spatiotemporal precision. The photoinduced temperature increase is at the basis of the photothermal therapy, which exploits the higher sensitivity of tumoral cells to 42–45 °C temperatures in comparison with healthy cells [2].

In this contribution, we report highly biocompatible Au nanostructures, formed through blue light irradiation of a novel β/γ -cyclodextrins branched copolymer, functionalized with a nitric oxide (NO) photodonor. It is shown that NIR absorbing Au plasmonic nanostructures can be rapidly synthesized exploiting only the photogenerated NO as reducing agent and avoiding the employment of any other surfactant or stabilizing ligand. Their photothermal properties and the stability over time are discussed and the preliminary biological tests on sarcoma cancer cell lines are reported.

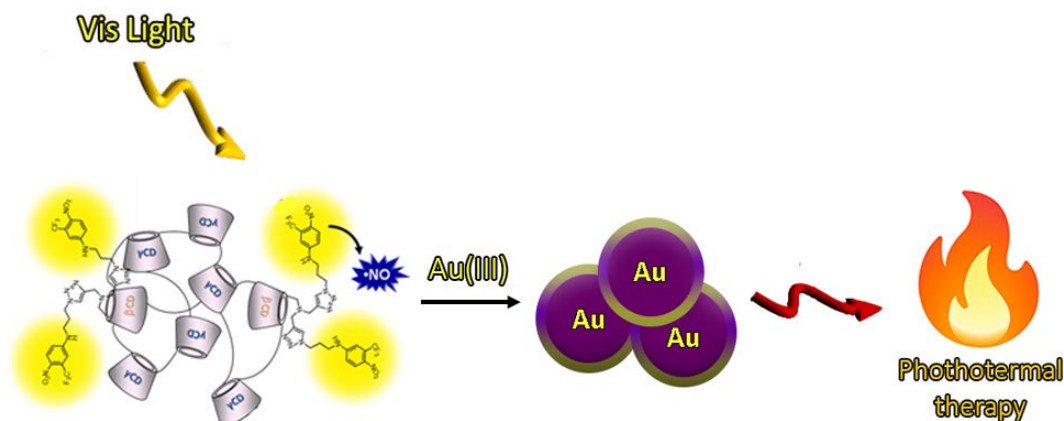


Fig. 1 – Schematic representation of the AuNPs formed from the copolymer under Vis-Light and generating heat by light stimuli.

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Isophthalonitrile derivatives as TADF-active chromophores for metallaphotoredox catalysis

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Photoredox catalysis has recently obtained increasing attention as a sustainable means for organic chemists, enabling the formation of suitable radical species through electron- or energy transfer.[1] Specifically, the merger of photoredox and metal-assisted catalytic cycles has rapidly gained popularity as an efficient strategy to open the way to new reaction pathways, especially those able to generate highly reactive nucleophilic species.[2]

Recently, [3-5] our attention has been focused on isophthalonitrile derivatives, an easily prepared class of organic dyes, whose uncommon photophysical properties have been studied in detail, together with their photo-redox behaviour. Upon visible-light excitation, these chromophores can show a long-lasting excited state as a consequence of a thermal-activated delayed fluorescence (TADF) deactivation. The analysis of photo-induced electron transfer kinetics in the presence of such chromophores and suitable quenchers guided us in the design of C-C bond formation reactions: allylation and propargylation of aldehydes mediated by *i*) a Ti^{IV} complex (titanocene dichloride) and *ii*) Bi^{III} salts have been successfully achieved, allowing access to a wide range of unsaturated alcohols in high yields in sacrificial conditions. Moreover, an enantioselective version of the same reaction, in the presence of chiral Ni^{II} complexes, has been developed.

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Thermal control of up-conversion process on silica capsules through incoherent excitation

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Since the field of solar harvesting is having a huge interest from the scientific community, we focus our attention on photon up-conversion (UC) process that allows to convert low-energy radiation into higher-frequency light. A versatile strategy to achieve UC emission is based on triplet-triplet annihilation (TTA) process taking into account two molecules: platinum-octaethyl porphyrin (PtOEP) as sensitizer and 9,10-diphenylanthracene (DPA) as emitter. TTA-UC is strongly sensitive to the presence of atmospheric oxygen, because it can reduce the decay time of the involved triplet states limiting the probability of the process.[1] A strategy to protect chromophores from molecular oxygen is the presence of unsaturated bond solvents [2] or the inclusion of dyes for TTA-UC in host matrix capable of protecting the couples and, at the same time, produce a solid device for real application. [3] In particular, in this work the molecular pair PtOEP/DPA has been studied in two isomers of fatty acids, elaidic and oleic acid, considered as phase change materials (PCM) allowing the UC efficiency control in response to the temperature [4]; indeed chromophores dissolved in PCM show temperature-controlled optical and photophysical properties, caused by the changes in the chromophore arrangements in liquid or solid medium. [5]

Firstly, the bulk solution has been prepared, then the organic dyes have been encapsulated in oil-core/silica-shell structures and, after optical and morphological characterization, the upconverted emission have been recorded under thermal control using an incoherent excitation source. The results have been rationalized in terms of aggregates, which having lower energy respect to the monomeric form, they prevent the triplet-triplet energy transfer (TTET) as reported in Figure 1, limiting the efficiency of the process. Finally, we have been also evaluated the different packaging of the two isomers through Raman spectroscopy which modifies the UC intensity.

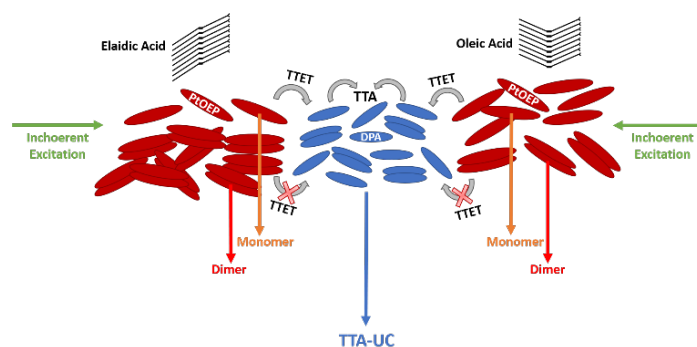


Figure 1 PtOEP/DPA up-conversion scheme based on TTA in oleic and elaidic acid.

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Dimethylazobenzene: A New Chemical Actinometer

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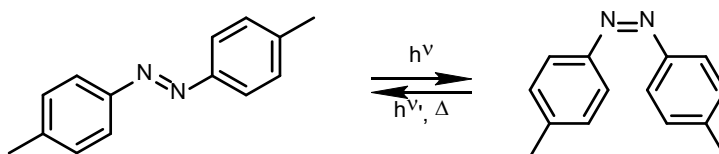
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Chemical actinometers are a useful tool in photochemistry, which allows to measure the photon flux of a light source to carry out quantitative analysis on photoreactions.[1] The most commonly employed actinometers so far show minor drawbacks, such as difficult data treatment, parasite reactions, low stability or impossible reset.[1] We propose herewith the use of *p,p'*-dimethylazobenzene (figure) as a chemical actinometer.[2] This compound undergoes a clean and efficient E/Z isomerization, approaching total conversion upon irradiation at 365 nm. Thanks to its properties, it can be used to determine the photon flux in the UV-visible region, with simple experimental methods and data treatment, and with the possibility to be reused after photochemical or thermal reset.



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Visible light-driven synthesis of symmetrical (hetero)biaryls by homocoupling of arylazo sulfones

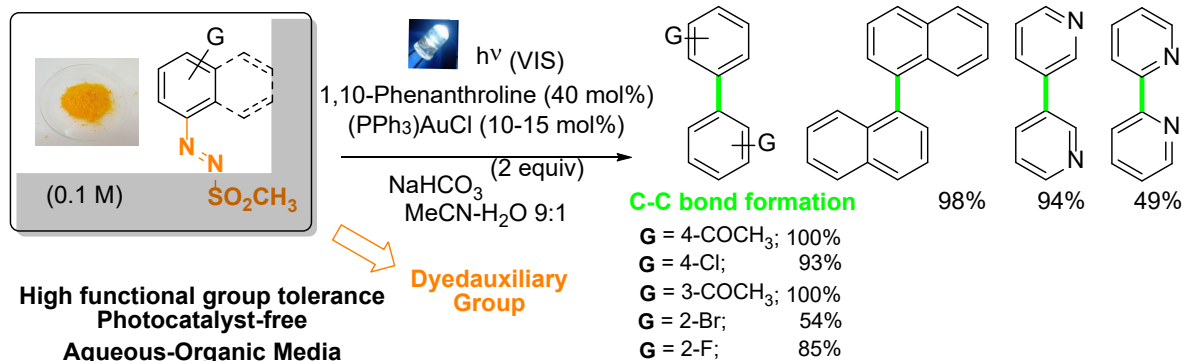
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Symmetrical biaryls have found interesting applications as precursors of rigid liquid crystals, semiconducting complexes and are present in several natural and artificial biologically active products.[1] Intense research on the preparation of these compounds started in the early 20th century with the development of the Ullmann coupling reaction. So far different leaving groups have been used to promote aryl-aryl bond formation starting from Ar-X compounds (e.g. X = I, OTf, N²⁺, etc.) making use of various transition metal complexes (including PdII derivatives) as the catalysts.[2] Recently, we focused on the photoreactivity of arylazo sulfones, (ArN₂SO₂CH₃), that are yellow to orange bench-stable compounds bearing a dyedauxiliary group (DG = N₂SO₂CH₃) which imparts both colour and photoreactivity to the molecule.[3]

We present herein a visible light-driven protocol for the (hetero)aryls homocoupling of arylazo sulfones under photocatalyst-free conditions by using (PPh₃)AuCl (10-15 mol%) and 1,10-phenanthroline (40 mol%) as catalyst and the ligand, respectively. The reaction is performed at room temperature upon visible light irradiation ($\lambda = 427$ nm) in a mixed organic/aqueous solvent and exhibits a high functional group tolerance. Biaryls and binaphthyls have been isolated in highly satisfactory yields.



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Visible Light Driven Cyclization for the Synthesis of 2-Functionalized Saturated N-Heterocycles

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Nitrogen saturated heterocycles have emerged as a promising class of bioactive molecules and attractive scaffolds for innovative drug design due to their new relevance as bioisosters of aromatic rings.

Although these cyclic molecules exceed their aromatic analogues in solubility, pharmacokinetics, and bioavailability,[1] their construction is still confined to a limited number of predictable synthetic methods. The commonly reported strategies towards these alkaloids depend on functional groups interconversion, resulting in processes characterized by low atom economy and waste production. [2] Therefore, the limited commercial availability and arduous functionalization of these compounds rise a major synthetic challenge.

In this scenario, we relied on the orthogonal and still unexplored reactivity offered by photocatalysis to propose an alternative and streamlined approach to pyrrolidines, piperidines and aziridines. Here, we describe an innovative new synthetic strategy towards various functionalized saturated *N*-heterocycles where blue light irradiation promotes a haloamination of allene C-C bond. The functional group of allenes, bearing two adjacent double bonds, allows a domino process to occur with an intramolecular cyclization followed by an intermolecular halogenation. Thus 1-halo-vinyl-*N*-heterocycles are delivered as products, providing a versatile lateral functional group (halo-vinyl moiety) for the otherwise still arduous further derivatizations of these nitrogen saturated heterocycles.

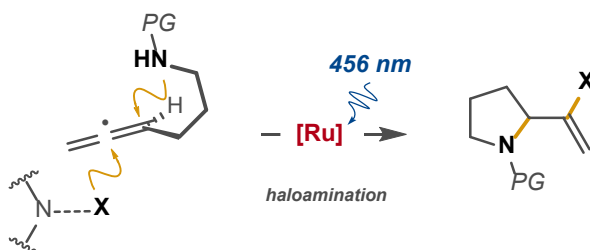


Figure 1. Visible light driven cyclization for the synthesis of functionalized saturated *N*-heterocycles.

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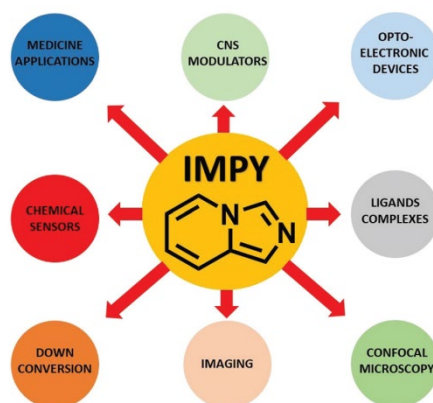
Emissive imidazo[1,5-a]pyridine scaffold: luminescent and versatile core for various applications

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In the last few years, the imidazo[1,5-a]pyridine core and its derivatives have attracted growing attention due to their unique chemical structure and versatility, optical behaviours, and biological properties. This class of aromatic heterocycles has great potential in several research areas, from materials science to the pharmaceutical field, and in recent years many promising innovations have been reported in different technological applications, such as optoelectronic devices, sensors, anti-cancer drugs, and emitters for confocal microscopy and imaging. The purpose of this presentation is to show the reported applications of a large variety of molecular products, comprising the imidazo[1,5-a]pyridine nucleus and our recent study concerning luminescent imidazo[1,5-a]pyridine ligands and corresponding transition metal complexes.[1–8]



In general, small molecules with large Stokes shift are acquiring great interest, due to their potential application as eco-friendly and low-cost products in down-shifting emissive layers, both in lighting and photovoltaic fields, as well as confocal fluorescence microscopy. Because of their features, imidazo[1,5-a]pyridines derivatives are particularly well suitable for employment in these fields.

On the other hand, as a ligand, the imidazo[1,5-a]pyridine skeleton can coordinate a large variety of transition metal ions, producing a great number of metal complexes in a great library of different coordination motifs, showing optical tunability, good solubility, intense emission and good quantum yield, strong pH dependence and good biocompatibility.

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Multifaceted role of Mo⁶⁺ doping in BiVO₄ photoanodes for solar energy conversion

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Among the most promising photocatalysts for solar energy conversion into hydrogen as a clean fuel via photoelectrochemical (PEC) water splitting, BiVO₄ has emerged as a leading candidate for the oxygen evolution reaction thanks to its relatively narrow bandgap of 2.4 eV, energetically low-lying valence band position and excellent internal charge separation [1]. In spite of these attractive features, the activity of BiVO₄ for water oxidation is severely limited by a slow hole transfer kinetics. So far, doping BiVO₄ with hexavalent metal ions such as Mo⁶⁺ or W⁶⁺ has been largely employed to increase the conductivity of the material by supplying additional free electrons [2].

In this work we demonstrate, through morphological, optical, and PEC investigations, that incorporation of the Mo⁶⁺ dopant plays a crucial role also on the surface properties of BiVO₄ electrodes, prepared as multilayer films with different doping degree through spin coating deposition of aqueous solutions of the precursors onto FTO substrates. A 3 at.% Mo⁶⁺ content was identified as the optimum doping degree providing the highest increase in PEC performance with respect to pure BiVO₄ under solar simulated irradiation through the film/electrolyte interface (Fig. 1), as a result of the greatly improved electron transport within the material bulk. Moreover, PEC impedance spectroscopy revealed that the Mo⁶⁺ dopant has a highly beneficial impact on the surface issues of BiVO₄ films, by passivation of the V⁵⁺/V⁴⁺ redox states acting as surface charge carrier traps that strongly limit the performance of the pure material for water oxidation, while not significantly affecting the much easier oxidation of the sulfite hole scavenger. A preliminary transient absorption spectroscopy study in the fast (fs–ns) timescale accounted for the peculiar impact of the adopted doping strategy on the charge carrier dynamics in BiVO₄ electrodes, depending on both the doping degree and the target oxidation substrate.

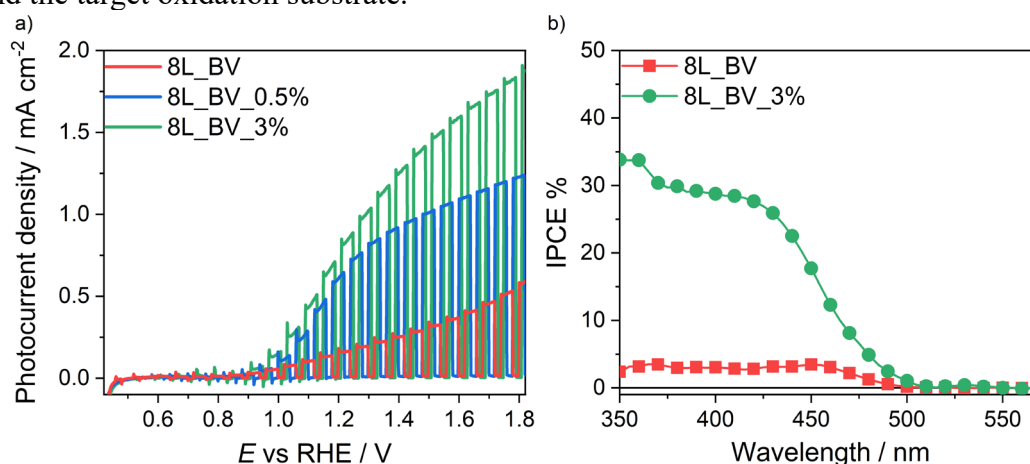


Fig. 1 a) Linear sweep voltammetry and b) incident photon to current efficiency (IPCE) plots at 1.23 V vs. RHE of pure (8L_BV) and Mo⁶⁺-doped BiVO₄ electrodes (8L_BV_X%) in 0.5 M Na₂SO₄ under AM 1.5 G front-side illumination.

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Micro- and nanoplastics: detection in water with a fluorogenic hyaluronan probe

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Each year hundreds of million tonnes of plastic waste are produced globally. Despite the increasing attention on its proper disposal and recycling, the largest part of this plastic waste has accumulated in the environment over the last five decades and continues to grow.

According to the ecosystem where it accumulates, this waste can be degraded into small debris (micro and nanoplastics) through different pathways¹ affecting the living organisms and, under many aspects, this represents a safety concern also for human health².

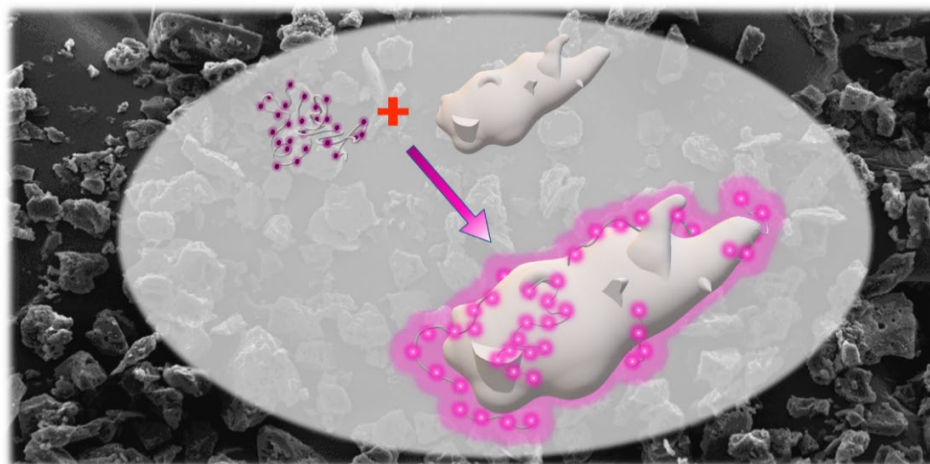
Importantly, the presence of the smaller-sized fragments, i.e., nanoplastics, drew major toxicological concern since they become more bioavailable and could interact directly with cells. While larger microplastics can be detected with different methods, the identification of units of micron and nano-sized fragments is a problem for which an efficient solution is urgently required.

In our work we studied the interaction with micro- and nanoplastics (MNPs) of a fluorogenic biopolymer based on hyaluronan functionalized with Rhodamine B (HA-RB).

In the probe alone the dyes are confined close to each other in hydrophobic pockets, where both inter- and intra-filament fluorophores interact to cause a massive fluorescence self-quenching.

Upon interaction with MNPs, occurring with high affinity, self-quenching interactions are broken, and HA-RB becomes brightly emissive. This fluorescence switch-on event allows to successfully detect MNPs with size down to the diffraction limit of confocal microscopy (ca. 250 nm). In addition, FLIM images show that fluorescence lifetime decays of the probe changes according to the different plastics, paving the way to differentiate the MNPs nature via fluorescence lifetime measurement.

Furthermore, HA-RB largely eliminates false-positive results caused by formation of dye aggregates as reported for different methods in literature, also yielding the high S/N ratio which allows the unequivocal detection of nano-sized fragments.



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The Evolution of Light Effected Autonomous Molecular Pumps

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The development of molecular devices able to operate autonomously away from equilibrium and perform tasks when an external source of energy is applied, still represents one of the major challenges in supramolecular chemistry, with very few examples available.[1] We reported a pseudorotaxane system which, upon light irradiation, acts as a molecular pump allowing the unidirectional transit of the thread through the macrocycle in a dissipative way, operating cyclically according to energy and information ratchet mechanisms (Fig 1a). [2] We recently demonstrated that slight variations in the structure of the axle component can enhance the performance of the motor and ¹H NMR spectroscopy allowed to observe the dissipative out-of-equilibrium state of the system under light irradiation. [3] Moreover, the pump module could be modified in order to introduce it in more complex architectures. Following focused design and modelling, a suitable phenylene derivative was identified to be used as an alternative pseudostopper. [4] The structure was therefore expanded to include a reservoir, which would allow to pump, and potentially trap, the macrocycles in a higher energy state once light of the appropriate wavelength is shined upon the system (Fig. 1b).

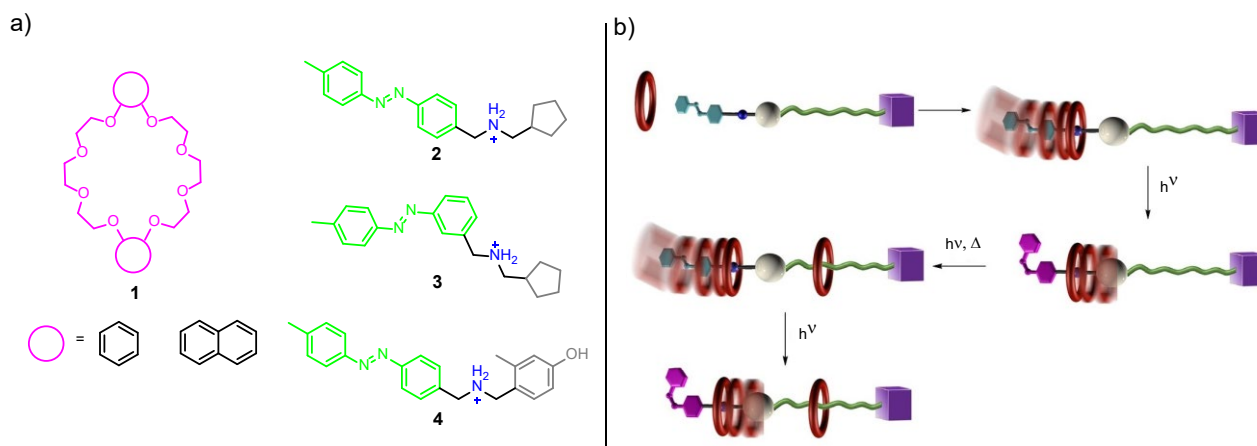


Figure 1- a) Structures of the components of the pumping module. b) Schematic representation of the reservoir modified pump operation mode.

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Improving light-driven molecular pumps: dissecting thermodynamic and kinetic entanglement in a photoswitchable molecular axle

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The development of molecular pumps able to operate autonomously far from equilibrium constitutes one of the major challenges of modern nanotechnology.[1] In principle, these nanoscale devices can be powered by a variety of energy sources, including electrochemical, chemical, and light energy.[2] Light-driven artificial molecular pumps based on (pseudo)rotaxane architectures have recently been realized in our laboratory.[3,4] The operation of our nanoscale pump is dependent on the light-induced modulation of the self-assembly between a crown ether macrocycle and a linear component consisting of a photoswitchable azobenzene unit and a dibenzylammonium unit, which is a recognition site for the rings. To optimize our system, it proved necessary to better understand the nature of the entanglement between the photoswitching of the azobenzene moiety and its thermodynamic and kinetic effects on the self-assembly of the ring and the axle. To achieve this, we developed a symmetric molecular axle in which the two key components of the pump module, i.e., the ammonium recognition site and the azobenzene unit, are separated by a short chain. The novel thread was characterized by means of ¹H NMR and UV/Vis spectroscopy. The formation of a supramolecular complex between the axle and DB24C8 crown ether was investigated in the dark and upon irradiation by means of mono and bi dimensional dynamic NMR spectroscopy. Our preliminary results highlight that the small structural variation introduced has nonetheless a large effect on the characteristics of the system. The results obtained suggest that the modulation of the kinetic and thermodynamic parameters induced by the photoisomerization of the azobenzene moiety in this type of systems is mediated not only by steric effects, as previously hypothesized, but also by inductive ones.

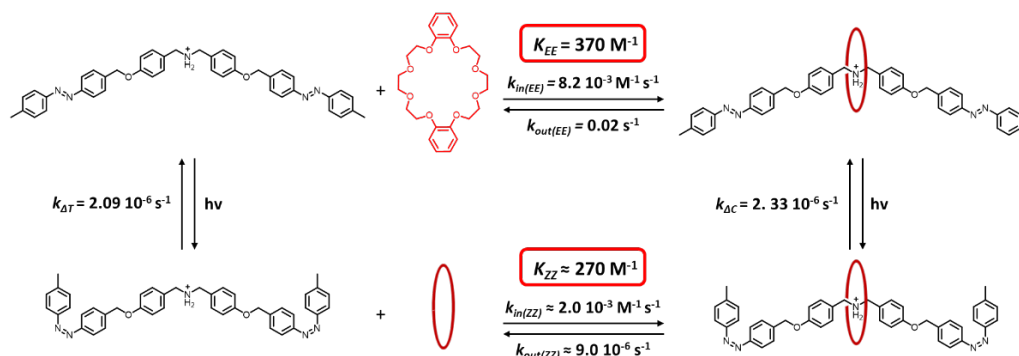


Figure 2: Structures of the components and operating cycle of the supramolecular complex.

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Dynamic and Thermodynamic Insights in the Operation of a Light-Fueled Supramolecular Pump

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Synthetic molecular systems operating autonomously away from equilibrium upon energy consumption represent one of the major challenges in modern supramolecular chemistry.[1] Their design and operation is, however, a fundamental step to be taken for gaining a deeper understanding of the dissipative networks of reaction that operate in living organisms. We recently reported on a series of supramolecular pumps capable of using light energy to shift a close reaction network away from its thermal equilibrium state.[2] NMR spectroscopy was used to observe the dissipative non-equilibrium state generated in situ by light irradiation.[2b,c] Thanks to our experimental setup we can monitor the system composition in the dissipative state, and we could probe a relationship between the light energy input and the deviation of the dissipative state from the equilibrium composition. Additionally, a detailed dynamic and thermodynamic characterization of the non-equilibrium state was possible for the first time in an artificial system. The rate and quantum yield of cycling, the energy storage in the system upon operation and the dissipation to sustain the non-equilibrium state, for four different incident light powers were extracted from experimental data. This study provides an unprecedented insight in the non-equilibrium behaviour of (photo)chemical reaction networks, and represents a significant step forward in the experimental characterization of dissipative states.

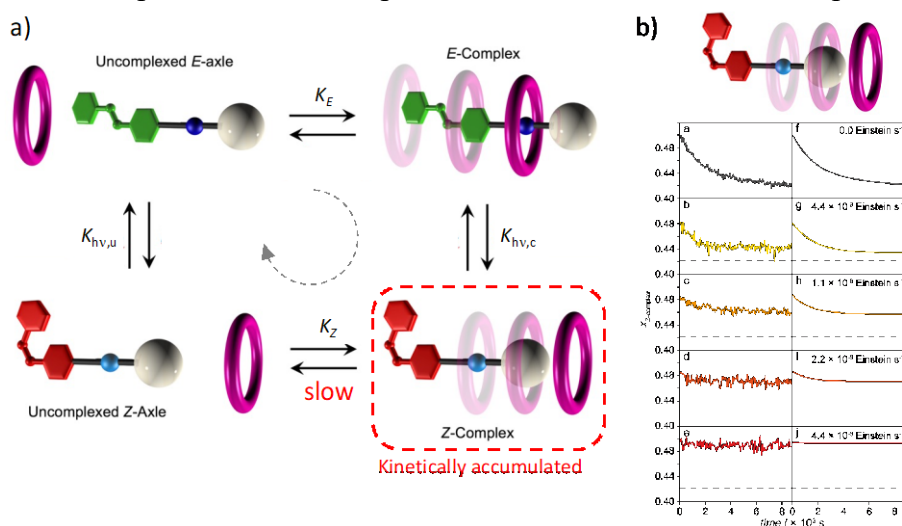


Figure 1. a) Closed reaction cycle travelled clockwise by the pump upon operation. b) Concentration of the kinetically trapped complex at different powers of incident light.

[1] a) M. Baroncini, S. Silvi, A. Credi, *Chem. Rev.* **2020**, *120*, 200–268; b) E. Mattia, S. Otto, *Nat. Nanotech.* **2015**, *10*, 111–119.

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Thiospherulene: Polysulfurated and Phosphorescent Molecular Cage

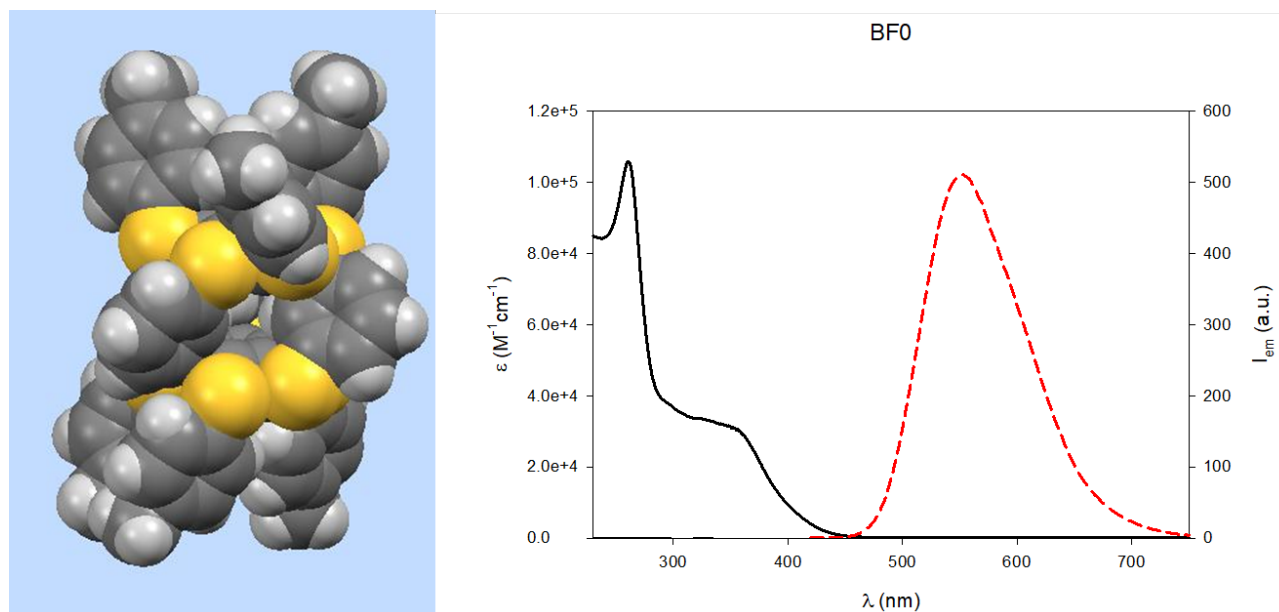
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Persulfurated compounds are not emissive in solution and usually highly emissive in solid state [1] or in rigid matrix, by freezing the solution or rigidification by chelation with metal ions [2] or encapsulation into silica nanoparticle [3]. Is possible to rigidify enough the structure, without an external stimulus, to obtain phosphorescence in aerated solution?

The synthesis of a thiospherulene (BF0), a polysulfurated molecular ball, assimilated to a polysulfurated and chiral cyclophane is the answer. The structure was confirmed by X-ray diffraction of a single crystal. In the solid state, a phosphorescence emission is observed with a high quantum yield. In a very interesting way, BF0 is also phosphorescent in solution, meaning that the locked structure is rigid enough to turn on the phosphorescence, slowing down the non-radiative deactivation of the phosphorescent excited state. This result is really interesting because this is the first example of a persulfurated molecule that exhibits phosphorescence without the aggregation induced emission mechanism. This property could be explained by the rigidity of the structure, in a similar way as when we rigidify the structure of persulfurated benzenes by complexation with metal ions [2] or by encapsulation inside a silica NPs [3]. The Thiospherulene BF0 could be the archetype of a new series of phosphorescent metal-free dyes.



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Acidochromism of first-generation Donor-Acceptor Stenhouse Adducts (DASAs): a pH-sensitive switch in halogenated solvents

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Switchable materials undergoing reversible structural changes in response to external stimuli have attracted considerable interest for potential applications as molecular switches, logic gates and sensors.[1] Donor-Acceptor Stenhouse Adducts (DASAs) are a new class of photochromic systems introduced in 2014 that isomerize from a colored triene form to a colorless cyclopentenone form (**1** and **2**, Figure 1a).[2] DASAs exhibit excellent photoswitching character with significant fatigue resistance, however these properties have been so far restricted to aromatic solvents.[3] In fact, there are only very few reports of efficient isomerization in halogenated solvents. In this work, reversible switching between the open and the cyclized form of a 1st generation DASA (**1**, Figure 1a) was achieved in dichloromethane via chemical stimuli, namely by acid-base additions. The addition of triflic acid to the DASA induces intense variations in the UV-vis absorption spectrum of the system: an instantaneous blueshift from 560 nm to 480 nm of the strong absorption band typical of DASAs is observed, which is then followed by a thermal process that leads to a complete bleaching of the visible-range absorption bands. These processes are attributed to an initial fast protonation of the open species, followed by a slow isomerization to the closed protonated cyclopentanone species. Then, addition of a strong base allows the recovery of the colored form with > 90 % yield. This study thus highlights the acidochromic properties (Figure 1b) of DASAs in halogenated media, which give to this system the potential to be exploited as pH-sensitive switch that can reversibly isomerize upon chemical stimulus.

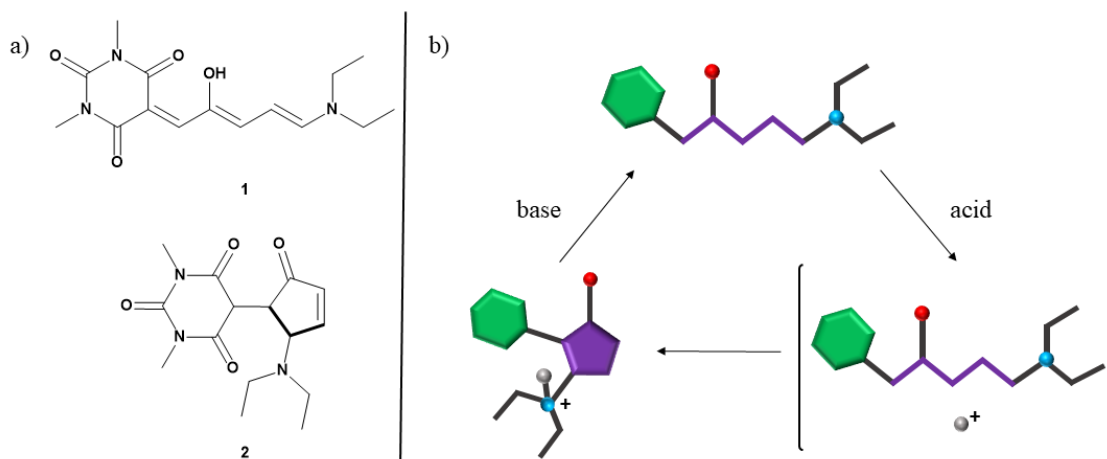


Figure 3. a) Chemical structures of the open and cyclized forms of a 1st generation DASA; b) schematic representation of the acid-induced isomerization reaction.

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Calix[6]arene-based rotaxane orientational isomers with distinct photophysical properties

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Calixarenes are a well-known class of supramolecular hosts and, within our group, heteroditopic calix[6]arenes have been extensively studied for their ability to bind axle-like molecules, such as *N,N'*-dialkyl viologens, to yield pseudorotaxanes and rotaxanes.[1]

Being the calix[6]arenes a non-symmetric wheel, the threading process can take place from the two different rims, possibly in a controlled way. When also the axle-like component is asymmetric, (pseudo)rotaxane orientational isomers can be obtained. These isomers are usually characterized by similar properties and their distinction is non-trivial.

It has been recently demonstrated that stilbazolium axles can thread calix[6]arenes yielding a mixture of pseudorotaxane orientational isomers with different emission spectra.[2]

We report the study of calix[6]arenes-based rotaxanes with stilbazolium stations. As for the pseudorotaxanes, the orientation of the wheel influences the stilbazolium properties while the interlocked structure allows the separation of the two isomers, enabling a thorough characterization. The Up isomer (see Figure 1) strongly enhances the emission of the station, even in solvents where the fluorescence of the stilbazolium is almost quenched. On the other hand, the Down isomer improves the photoisomerization of the central double bond, making this process more pronounced and stabilizing the *Z* isomer.

In conclusion, the encapsulation of the stilbazolium moiety in the calixarene cavity can be used as a method to enhance, in a supramolecular way, different and complementary properties of the stilbazolium, depending on the orientation of the macrocycle.

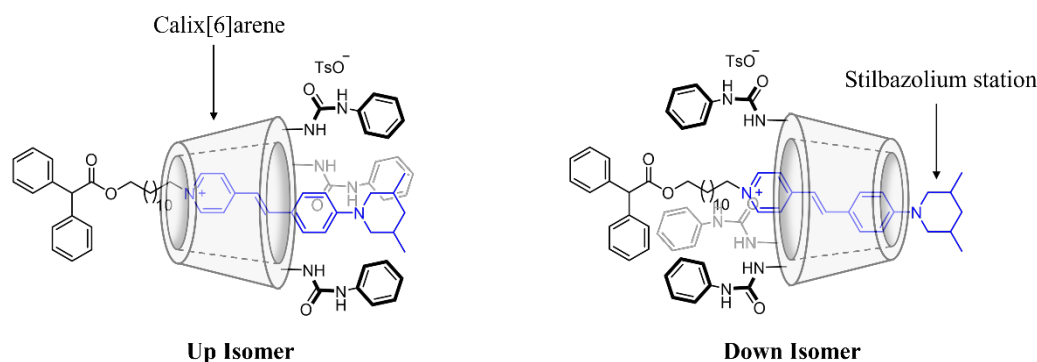


Figure 1. Schematic representation of the [2]rotaxane orientational isomers

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Singlet Fission Footprints in a new class of Fluorene Derivatives: Charge-Transfer Mediation and Possible Implications

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Singlet fission (SF) is a rare exciton multiplication phenomenon in which a singlet excitation is down-converted into two independent triplets [1,2]. As from one-photon-absorption event two charge carriers can be generated, SF gains great application potential promising to overcome the Shockley-Queisser limit for the external quantum efficiency of a single-junction solar cell (34% for a common silicon-based solar cell) [3]. Experimental evidence for SF in a new class of small fluorene-based molecules, featured by two-branched donor-acceptor structures, was detected for the first time in solution [4]. Femtosecond time-resolved spectroscopy unveiled the ultrafast formation (occurring in few picoseconds) of an intriguing precursor of the triplet excited state, showing analogous triplet-like spectral profile, assigned to the double triplet intermediate of SF [5]. Then, a detailed study of the concentration effect on triplet quantum yields revealed efficient triplet exciton production, up to 145%, in the more concentrated samples. The determination of the triplet energy addressed by sensitization and phosphorescence experiments jointly to quantum mechanical calculations at TD-DFT level of theory allowed to draw the energy level diagrams, used to verify the thermodynamic feasibility of the SF phenomenon.

Furthermore, to gain insight into the plausible SF mechanism, the solvent polarity effect and the role of intramolecular charge transfer (ICT) have been thoroughly explored with several advanced spectroscopies. The experimental results suggested that the push-pull character strongly favors SF, as long as the ICT state is virtual, while it opens competitive channels when acting as trap in the more polar environment [6].

The unconventional property of generating high-energy triplet excitons (ca. 2 eV) via SF makes these photostable fluorene-based materials outstanding candidates as photosensitizers or charge extractor for photovoltaic devices. Their potential applicability thus triggered the preliminary investigation of fluorene solutions in presence of well-known electron-acceptors, namely fullerene (60-PCBM) and N,N'-diphenyl-3,4,9,10-perylenedicarboximide, carried out through steady-state and time-resolved spectroscopy, in order to gaze the possible electron-injection process. In addition, preparatory studies on thin films paved the way for further possible implementation in solid-state devices.

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Electrodes and electrolyte materials for aqueous dye-sensitized solar cells

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Third generation photovoltaic (PV) has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be considered in any PV technology is the stability under real outdoor conditions, as well as the sustainability of materials/components and the facile integration with energy storage systems.

In the last five years, dye-sensitized solar cells (DSSCs) with water-based electrolytes have been considered as one of the possible breakthroughs towards DSSC large-scale diffusion [1]. In fact, the replacement of the organic electrolyte ensures better stability and safety. If opportunely developed and optimized, aqueous solar cells can be truly considered a low-impact photovoltaic device with non-toxic components [2].

Herein, we show our last results on this field, such as the possibility of gelyfing the electrolyte into a solid matrix and the replacement of Pt cathodes with conductive polymers or biomass-derived carbon substrates could increase the long-term stability and lower fabrication costs. Also, we report morphological modifications of TiO₂ photoanodes, introduced by adding various kinds of additives, both molecular and polymeric, to the commercial Dyesol TiO₂ paste, typically used for screen printing DSSC electrodes onto conductive glass [3]. It was found out that the addition of polyethylene glycol (PEG) modified both the morphology and the thickness of photoanodes. As a result, PEG-based cells showed an increased short-circuit current density (+18%) and power conversion efficiency (48%) with respect to the pristine counterpart.

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Study, characterization and comparison of photovoltaic devices both for indoor and outdoor application

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The use of small sized drones, arduino-based systems, Internet of things (IoT) and electronic digital devices has been rapidly growing in the past few years. Especially IoT connects numerous devices, such as wireless sensors, actuators, and wearable devices, to optimize and monitor daily activities. Most of these devices require power in the microwatt range and operate both indoors and outdoors. To this end, a self-sustainable power source, such as a photovoltaic (PV) cell, which can harvest both low-intensity and high-intensity light, for indoors and outdoors application, respectively is appropriate. Therefore, we compared two different types of PV devices, such as silicon and dye-sensitized solar cells, for harvesting in two different light condition (indoor and outdoor). With the aim to develop low-cost, stable, and efficient PV cells for indoor /outdoor applications, extensive investigation is necessary to resolve some critical issues concerning PV cells, such as large-area fabrication, environmental stability, mechanical flexibility, lifetime and fabrication cost. In addition, the biocompatibility of these devices should be improved through the development of new, non-toxic materials [1]. To address these issues, a systematic review of these aspects will be highly useful to the research community. We have already achieved a satisfactory power conversion efficiency of these solar cells in the indoor/outdoor environment.

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CdTe-QDs capped with plant biomass extracts: luminescence characterization

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Luminescent colloidal semiconductor nanocrystals, also known as quantum dots (QDs) have interesting size dependent properties which are useful for a wide range of applications ranging from PV-devices or photodetectors to bio-labels [1]. In the colloidal synthesis of nanomaterials, the size of the quantum dots can be controlled by the surface stabilization using different capping agents [2]. The capping agents not only play a crucial role in tailoring the size, shape, crystal structure and growth rate during the synthesis of QDs, but also affects their optical and/or electronic properties [3]. Plant derived chemicals and, more precisely, waste biomass extracts have been employed for ecofriendly, simple, rapid, stable and cost-effective production of nanoparticles [4]. Catechins are a class of flavonoids predominantly found in foods and beverages, such as apples, chocolate, red wine and green tea, as well as in many crop residues and plant wastes [5]. Currently, there is much research interest in catechins for their excellent antioxidant activities and biological properties. But they have also good chelating properties for metal ions [6-7]. In the present work we synthesized CdTe-QDs in aqueous solution [8] using catechins as a capping agent. To reach this goal we first tested the chelating capabilities of catechins by adding them to previously synthesized CdTe-QDs bearing 3-mercaptopropionic acid as capping. Then, synthetic procedures using only catechins as a capping agent were carried out. All samples were fully characterized by monitoring their luminescence properties.

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Hybrid luminescent materials based on silicon nanowires and Ru(II) and Os(II) polypyridine complexes

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The fabrication of low-cost silicon (Si)-based light-harvesting antenna systems using industrially compatible technology is a goal with enormous impact, because these devices represent a valid alternative for novel and challenging applications. Recently, the efficiency of Si nanowires (Si NWs) as energy donor and multinuclear metal complexes as energy acceptor in a hybrid antenna system has been demonstrated for the first time by our research group. [1]

Here we report the preparation and study of hybrid luminescent materials as light-harvesting antenna system, made of Si NWs and multinuclear metal complexes, that emit in the near infrared (NIR). Complexes of the type [(L)Ru{(μ-2,3-dpp)Os(bpy)₂}₂][PF₆]₆ (where bpy = 2,2'-bipyridine, 2,3-dpp = 2,3-bis(2-pyridil)pyrazine, L = bpy or (4,4'-dicarboxy)bpy) have been synthesized and characterized. These chromophores show significant absorption throughout a broad range of the visible region, and their emission is located in the NIR region.

Through a detailed study of the optical properties, a process of energy transfer from NWs to the metal complex is here discussed into details. The realization of these novel hybrid materials based on the luminescence of ultra-thin Si NWs,[2] prepared by a MACE process, and dyes demonstrates the potential of these structures as very efficient hybrid antenna systems, paving the way for several strategic applications from photonics to photovoltaics, sensors and bio-imaging.

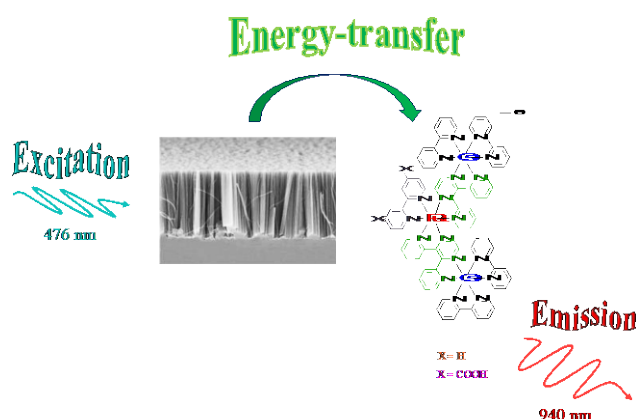


Fig. 1. Schematization of EnT process in a Si NWs (donor)/metal complexes (acceptor) system.

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Proton-coupled electron-transfer pathways involving cobalt-aquo/hydroxo sites of cobalt oxide nanoparticles and cobalt polyoxometalates

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Light-driven water splitting with production of hydrogen represents one of the most promising solutions to the global energy issue.[1] Within this framework, the quest for active and efficient catalysts, capable of stabilizing redox intermediates, turns out to be an extremely important task, particularly as far as water oxidation is concerned. This issue requires a suitable control of both electron and proton motion (proton-coupled electron-transfer, PCET) and the fundamental understanding of such process is thus of remarkable importance towards the optimization of the catalytic routine.[2] In the present communication we compare the primary PCET step involving either cobalt oxide (Co₃O₄) nanoparticles or a cobalt polyoxometalate polyanion (Co₆(H₂O)₂(α -B-PW₉O₃₄)₂(PW₆O₂₆)¹⁷⁻) and the photogenerated Ru(bpy)₃³⁺ oxidant (bpy = 2,2'-bipyridine).[3,4] Interestingly, although cobalt polyoxometalates are often identified as “molecular metal oxides”, we show herein that different PCET mechanisms and kinetics regimes are operating. Potential implications towards light-driven water oxidation catalysis will be discussed.

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Optimization of the platinum deposition process on sensitized NiO

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Water splitting exploiting solar energy could be a great solution to obtain green hydrogen, since solar is an extremely clean, cheap and largely available energy source [1]. In this framework, the use of semiconductor-based devices provides an easy way to directly convert sunlight into solar fuels. Taking inspiration from the dye-sensitized solar cell (DSSC) architecture, the use of sensitized wide-band gap semiconductor has recently appeared as a promising strategy [2].

In this work we studied photocathode systems based on nanostructured NiO semiconductor sensitized with an organic molecule (P1) and Pt as the hydrogen evolving catalyst (HEC) to promote the direct photoreduction of protons to hydrogen with concomitant oxidation of water at the counter-electrode [3,4]. Specifically, the main goal has been the optimization of the deposition of the Pt catalyst by adopting different photo(electro)chemical approaches as well as different types of NiO films. The photoelectrochemical activity of the resulting photocathodes has been studied by means of chronoamperometry and linear sweep voltammetry under chopped irradiation as well as by determination of the incident photon-to-current efficiency (IPCE). Interestingly, the performances strongly depend on the type of NiO substrate, the Pt deposition method, and by the combination of both, suggesting that the control of the film morphology, of the amount of sensitizer adsorbed, and of the growth of Pt clusters altogether play a fundamental role. Perspectives towards the development of novel photocathodes will be discussed accordingly.

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Blue Light Enhanced Heck Arylation of Allenes

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Between the most important tools of modern organic chemistry, transition metal-catalysed reactions have a prominent role. In the last years the already wide reactivity of metals as catalytic species has been farther broadened thank to the last developments in photocatalysis. In fact, the combination between classical organometallic catalytic systems (Ni, Co, Cu, Pd) and light has opened the way to an orthogonal and unconventional reactivity never achieved before. [1-3]

In this framework, we presented a synthetic strategy to obtain arylated vinyl pyrrolidines and piperidines starting from *N*-tosylaminoallenes. Key to the process was the usage of the blue light which allowed the efficient exploitation of the simple catalytic system Pd(OAc)₂/2PPh₃ at room temperature. Electron-donating, electron-withdrawing aryl and heteroaryl bromides were coupled with allenes in a Pd(0) catalysed cross coupling. A subsequent domino cyclisation triggered by the tosylamino functionality afforded valuable branched vinyl pyrrolidines and piperidines. Mechanistic investigations were realized in order to understand the role of the light in the catalytic cycle revealing the light to have a prominent role in the carbo-palladation step.

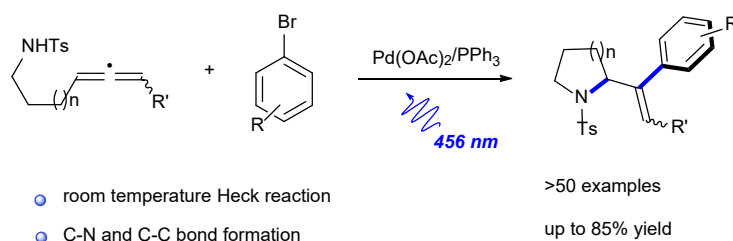


Figure 1. Visible light driven cyclization for the synthesis of functionalized saturated *N*-heterocycles.

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TADF chromophores in photoredox catalysis

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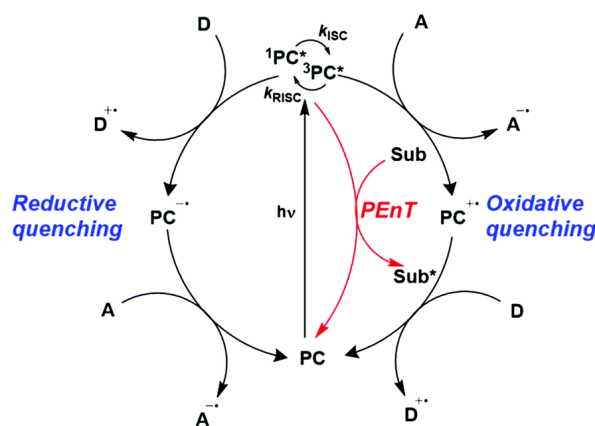
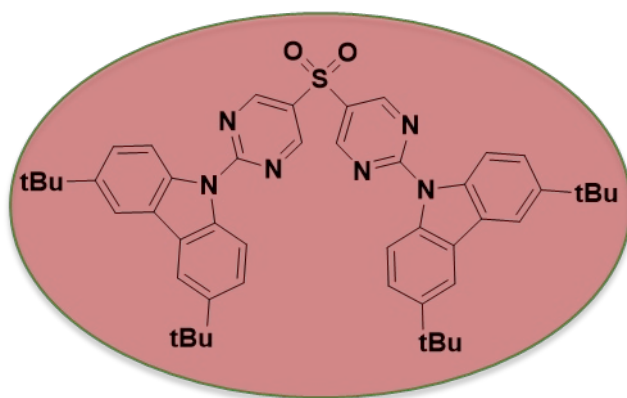
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Organic molecules with thermally activated delayed fluorescence (TADF) attract increasingly more attention in recent years as a class of functional materials. Especially after Adachi et al. introduced high-performance TADF-OLED devices in 2012 [1] design and synthesis of new TADF emitters has become a rapidly developing research field.

TADF stands for Thermally Activated Delayed Fluorescence because the S_1 and T_1 states are designed to be close in energy to achieve reverse intersystem crossing (RISC). Thus, excitons populated in T_1 state undergo a thermally assisted RISC to the S_1 state where they can then radiatively decay to the S_0 resulting in delayed fluorescence. TADF emitters have a great importance in the context of organic electronics because you can take advantage of the population of both S_1 and T_1 states.

The reported organic TADF materials are based on highly efficient Metal–organic complexes however pure organic TADF-based materials hold great promise for practical applications since they are relatively easy to modify. The potential of TADF compounds, such as **4CzIPN** or **pDTCz-DPmS**, as photocatalysts is of particular interest as the property of TADF results in comparable excited state lifetimes to heavy metal photocatalysts.[2] Therefore, we study a series of reaction employing **TADF emitters as photocatalysts** including decarboxylative addition of a proline protected compound to diethyl maleate.



This research has been financially supported by the PhotoReact ITN project within a collaboration with Zysman-Colman research group (University of St. Andrews, UK).

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Development of nucleophilic-sensitive and 3D printable polymeric materials employing cNDI dyes

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3D printing had a great and fast development in the last 30 years, both in academic and industrial fields. Among the different additive manufacturing technologies, Digital Light Processing (DLP) enables the fast construction of complex geometry through layer-by-layer controlled photopolymerization of liquid formulations. Typically, the liquid formulations include photocurable monomers/oligomers, a photoinitiator, fillers, and dyes. The role of the dye consists in competing with the photoinitiator to absorb the light, slowing down the photopolymerization process and thus enhancing its control, allowing better printing resolution [1]. In the last years, new research approaches have been devoted to the possibility of taking advantage of functional dyes that may both improve printing resolution and provide new features in the final object. Some examples are coumarins and azo-dyes, which are used to tune different properties of the 3D printed objects under external stimuli, such as light and temperature [2].

Herein, NDI-OH has been investigated as a functional dye for DLP 3D printing to impart pH-sensitivity properties to the materials. NDI-OH is a diprotic dye which can show three stable species (protonated/mono-deprotonated/bi-deprotonated) with different colors, spanning from yellow, to red to blue [3].

First, different photocurable monomers were compared to select the most suitable combination with NDI-OH in terms of miscibility, photopolymerization kinetics, and ability to show a fast and clear color change under a pH variation. The selected formulation resulted printable with very good resolution and CAD fidelity, and the material showed an evident sensitivity to pH conditions. Furthermore, it is also demonstrated that the 3D printed structures show a response both to liquid and vapor water solutions, as well as to organic solution containing DBU (Fig. 1), a Lewis bases. This great versatility can be used to employ the 3D printed devices in a wider range of applications than standard pH indicators as polymeric optical sensors.

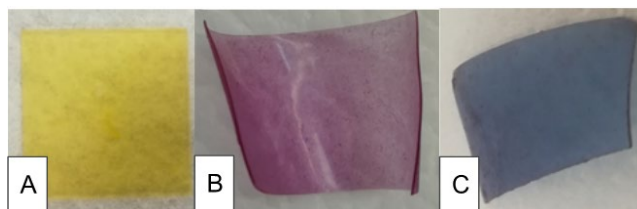


Figure 1. Color change before (A) and after the contact with DBU/*n*-Hexane solutions (B: 0.4% DBU, 24 hours; C: 5% DBU, 17 hours).

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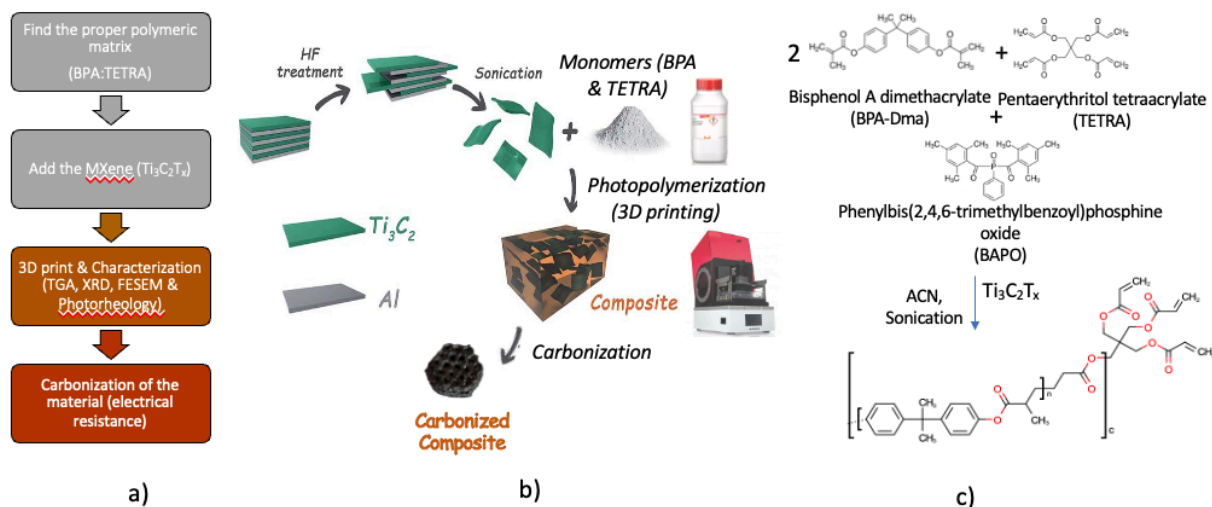
Introducing MXenes to 3D printed polymer nanocomposites for further electronic applications

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MXenes are a family of 2D nanomaterials with electrically conductive properties, hydrophilic and great dispersibility, made from transition metal carbides, nitrides or carbonitrides[1] presented in a multi-stacked or single sheet form[2]. This study focuses on the introduction of $Ti_2C_3T_x$ MXene on a specific polymeric composite formulation from BPA-DMA (Bisphenol A dimethacrylate) and TETRA (Pentaerythritol tetracrylate) for DLP-3D printing and its characterization. The characterization was performed for the nanocomposite under normal conditions and after a thermal treatment or carbonization, to distinguish its properties under reduced organic content. Thermogravimetry, XRD and FESEM were used for analyzing the material under both conditions, meanwhile, photorheology was used for studying the impact of the $Ti_2C_3T_x$ MXene on the photopolymerization. Furthermore, 3D scanning was also performed to determine the definition of the printed structures and their potential to reach complex configurations for later applications. These structures can have potential use in photo/electro-catalysis and energy applications.



a) Shows the flux that the investigation has followed. b) Graphic description of the laboratory process for the MXene/composite development. First part shows the synthesis of the MXene and then, the inclusion of the monomers for the *in situ* photopolymerization (This image has been adapted from Cao *et al.* *RSC Adv* 2017[3]) c) Chemical representation of the polymeric synthesis.

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Light-induced shape-memory polymers

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Stimuli-responsive compounds are an emerging class of new materials, able to respond to an external stimulus by changing mechanical, optical, or chemical properties. Among others, shape-memory polymers (SMPs) are attracting the attention due to their ability to transform from a programmed temporary shape achieved by mechanical deformation of the initial shape, back to the initial permanent shape upon exposure to a suitable stimulus. Traditionally temperature is the most common stimulus applied to induce shape recovery, heating the sample above its glass transition temperature. Light, electric, or magnetic fields can be also applied to induce this transition.[1] Additive manufacturing is an innovative way to produce shape-memory devices and digital light processing (DLP) is the most promising one able to achieve very high fidelity to the CAD virtual project and excellent final resolutions. DLP is a vat-photopolymerization 3D printing technique in which liquid photopolymerizable inks are employed. These polymers can find wide applications in smart fabrics, biomedical, electronics, packaging, aerospace, and many others in rapid expansion, thanks to recent growing interest in these polymeric devices.[2]

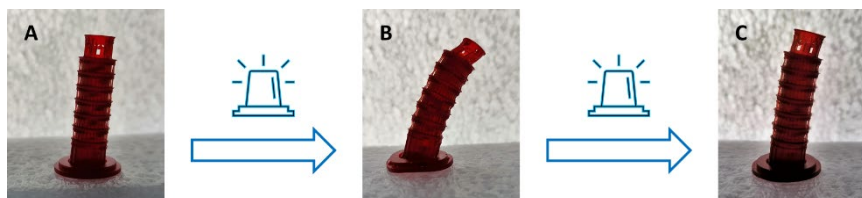


Figure: A) Original 3D printed shape of Pisa Tower; B) Temporary shape obtained after 5 minutes LED irradiation and mechanical deformation; C) Shape recovery after 5 minutes LED irradiation

Here we synthesize a series of azodye-based monomers functionalized with different groups able to absorb in a wide range of visible light. Low quantities (0.1 wt.%) of these monomers in the formulation of the inks allow to achieve very good results in term of high fidelity to the virtual structure and high resolutions. Moreover, through the introduction of a dye we can confer light-responsive properties, remotely controllable using a 459 nm LED irradiation. Finely tuning the light wavelength, intensity, and focus, selected areas can be irradiated, reaching high temperatures that can overcome in few minutes the second order transition temperature.[3] In this way, we are able to confer a temporary shape to the final device and then, exposing it under LED irradiation again, the initial shape is almost totally recovered without any visible damages to the polymer structure. Moreover, this process is very fast, and it can be repeated many times. This work presents therefore an innovative and tunable system in which the use of fillers is avoided, widening possible applications of the resulting devices.

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Fluorescent switch operating in a biphasic system

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Rotaxane-based fluorescent molecular switches are systems which combine a fluorescent moiety with the stimuli-responsive behavior typical of mechanically interlocked molecules (MIM). In 2008, Zhou et al. operated an anthracene-based multilevel molecular switch based upon protonation/deprotonation of a conjugated amine.[1] Recently, Wu et al. reported on a switchable BODIPY-based rotaxane, in which the on/off states were controlled by the mechanical hindrance around the fluorophore.[2]

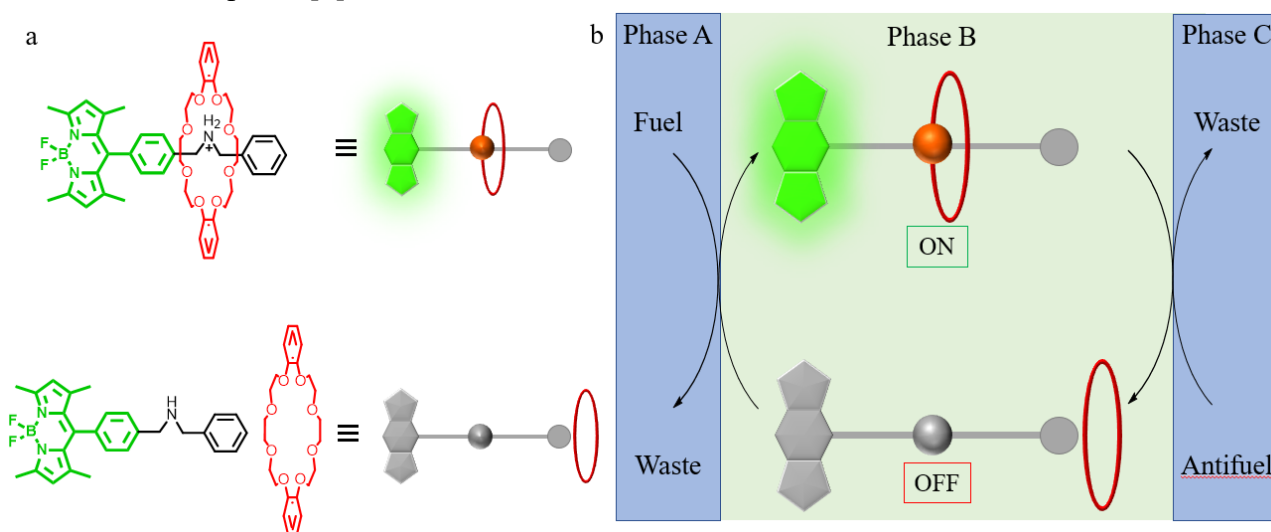


Figure 2. Schematic representation of the structure and operation of the developed fluorescent switch system.

In this project, we designed a BODIPY-based axle endowed with a secondary amine which is able to complex a crown ether ring upon protonation yielding a pseudorotaxane architecture (Figure 1, a). While in the deprotonated state the axle does not thread through the crown-ether and the fluorescence of the BODIPY stopper is quenched through energy or electron transfer from the free amine. Upon protonation, the fluorescence of the BODIPY moiety should be switched on due to a reduction of the electron-donating ability of the amine group. Thereby, in this system the fluorescence readout is directly linked to the molecular switch state (Figure 1, b). We plan to operate this molecular switch in a compartmentalized system, that is, separating the molecular switch, the fuel (an acid), and the antifuel (a base) into different phases. By placing the switch in the organic phase whereas leaving the acid and base in aqueous media, we can expect accumulation of the waste product exclusively in the latter. Furthermore, this approach should allow autonomous operation of the switch, which effectively acts as a phase-transfer catalyst for the reaction between fuel and antifuel, with the non-trivial result of converting a simple molecular switch into a full-fledged molecular machine.

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Novel perimidine-based squaraine dyes as cell membrane probes: a structure-function investigation in liposomes

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The efficient imaging of biological membranes is crucial in chemical biology. Membrane properties as well as the specific interactions happening among phospholipids, proteins and channels, are important to shed light on crucial biochemical pathways. In this context, near-infrared (NIR) emissive probes have recently attracted an increasing interest.[1] Small organic fluorescent compounds are promising candidates as stain of cell bilayer membranes, allowing a precise location within the membrane along with the possibility to fine-tune their photophysical properties by simple structural modifications.[2] In particular, NIR probes exhibit remarkable brightness, deep tissue penetration, poor biological toxicity and limited autofluorescence.[3]

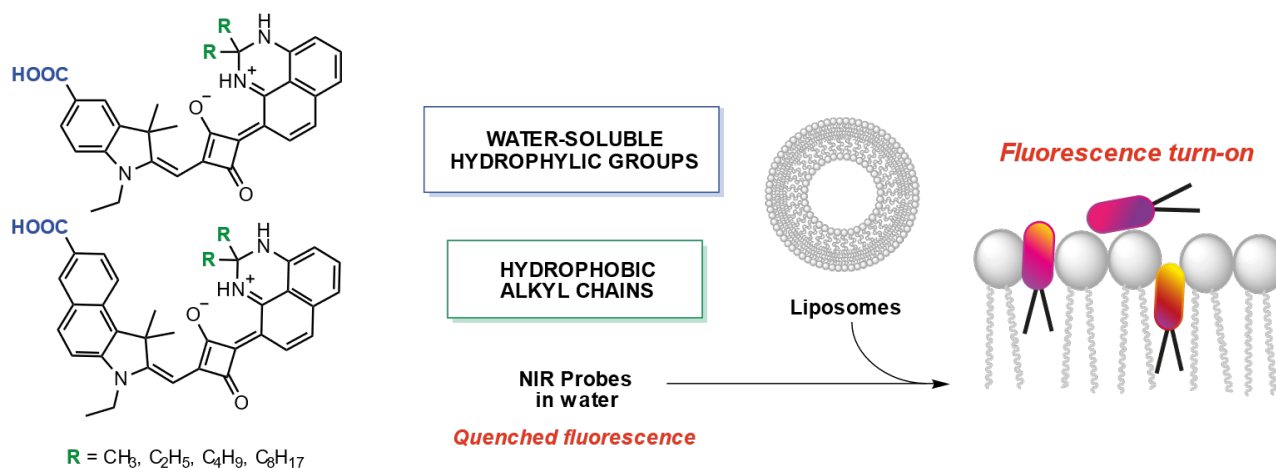


Figure. Representation of the interaction between the synthesized NIR probes and liposomes.

Although several emitters have already been proposed for this purpose, in this work a systematic structure-to-function study for novel bilayer membrane NIR probes is described. Two novel series of unsymmetrical squaraines based on indolenine and benzoindolenine have been synthesized. Alkyl chains of different length decorate the perimidinium core tuning the interaction of the probe with the liposome while a carboxylic group was linked on the other side of the structure to improve the water solubility. The photophysical properties and the kinetic of the probes' intercalation inside the bilayers has been monitored and evaluated in respect to the probe structures. The effect of the membrane phase and fluidity on the interaction has been evaluated too, providing a complete analysis about the key structural motifs for the design of novel NIR probes.

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Investigation of DASA properties in liposome

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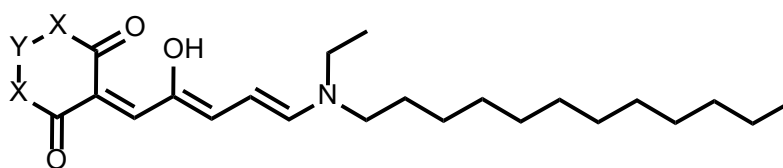
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Photochromes are molecules that can be reversibly switched between two forms by means of light. The variation of properties between the two isomers, especially when different polarities are observed, have been often used to trigger the behaviour of molecular compounds or materials. Most of the time, photochromes require high-energy UV light for their transformation which reduces their use, especially for bio-medical applications. On the contrary, Donor–Acceptor Stenhouse Adduct (DASA) can switch from an open coloured form to a closed colourless form with low energy light stimulation [1]. The photoisomerization induces not only a change in the absorption properties but also a drastic evolution of the polarity with a hydrophobic to hydrophilic transition triggered by visible light. These changes open the way for multiple applications of these new photochromes such as membrane or phase transfer.

If some properties of DASA in organic solvents have already been described, their behaviour in more complex environment, such as liposome still need to be explored [2].

In this contribution, we will outline our recent studies on the behaviour of symmetric and asymmetric DASA in liposomal formulation.



Meldrum's acid based DASA
M2-12: X = O, Y = C(CH₃)₂,
B2-12: X = N(CH₃), X = CO, Barbituric acid based DASA

Figure1: Molecular Structure of DASAs M2-12 and B2-12

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Naphthalene diimides organic emitters for artificial fluorescent proteins: a sustainable approach toward white Bio-Hybrid LEDs

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Bio-phosphors are promising candidates to replace rare-earth based down-converting filters in white light-emitting diodes. [1] Fluorescent proteins (FP) represent up-scalable and sustainable materials with remarkable photophysical features in both aqueous and polymeric environments. [2,3] Unfortunately, their natural chromophore undergoes to a prominent *cis-trans* isomerization under operative conditions undermining their extensive use in optoelectronic devices. In this context, novel artificial fluorescent proteins can be designed simply by replacing the natural chromophores with suitable small organic emitters. The advantages of the organic synthesis (*e.g.*, tunability of photophysical properties by simple structural modifications, up-scalability and low cost) are combined with the benefits of the peptidic scaffold (*e.g.*, aggregation-induced quenching avoided) for the realization of high-performances white Bio-LEDs.

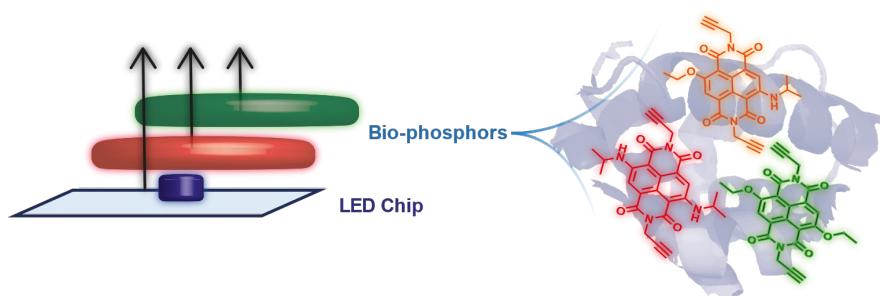


Figure: White LEDs architecture and first generation of prepared NDIs.

In this work, naphthalene diimides (NDI) chromophores were investigated by simultaneously operating on both the aromatic core and on the imide moieties. The former was addressed on the insertion of different donor moieties to tune the fluorescence features from green to orange to red. The latter consisted of the functionalization with a reactive alkyne group on the edge imide suitable for specific and selective bioconjugation with the protein scaffold. The photophysical properties and the photostability of these dyes in LED operative conditions have been investigated, showing promising results and providing remarkable insights to better tune and improve the dyes features in the final devices

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Photochemical synthesis and preliminary photophysical evaluation of a multi-component polymer enabling PDT in hypoxic conditions as novel Breast Cancer treatment

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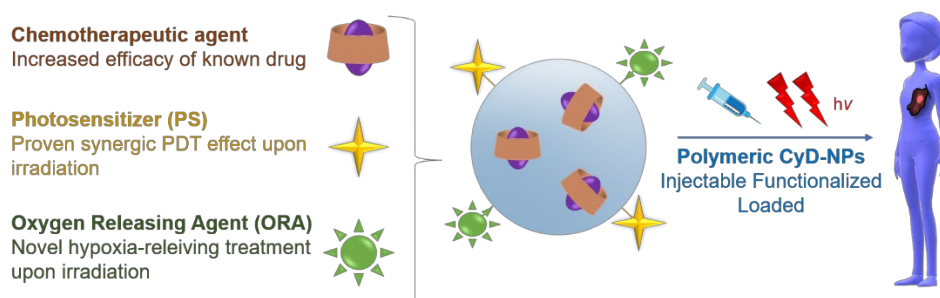
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Nanotechnologies grounded on cyclodextrin (CyD)-based polymeric nanoparticles (NPs) have been accurately tailored in order to improve the pharmaco-kinetic and dynamic profiles of conventional drugs and to load in a single, biocompatible carrier multiple therapeutic agents to achieve specific tumor tissue targeting [1]. Light-activated therapies are receiving increasing attention for the treatment of solid tumors, including Breast Cancer (BC). Photodynamic therapy (PDT) consists in the administration of a photosensitizer (PS) which produces reactive oxygen species (ROS) *i.e.* singlet oxygen ($^1\text{O}_2$), upon irradiation with red light in the presence of molecular oxygen (O_2), triggering a cascade of processes eventually killing cancer cells. Yet, tumor cells can undergo tissue hypoxia, such as an inadequate supply of O_2 , which will reduce PDT efficacy [2], and activate molecular pathways inducing resistance to chemotherapy (*i.e.* taxanes)[3].

The *HypoCyclo* project aims to optimize a novel combination of chemo- and photo-therapy for the selective and effective treatment of BC. CyD-based NPs able to load taxanes will be decorated with a PS *i.e.* Chlorin e6 (Ce6) and implemented with an Oxygen Releasing Agent (ORA) that will supply O_2 *in situ* [4].

We synthesized four anthracene and naphthalene derivatives known as suitable ORA because of their capacity to form endoperoxide moieties by trapping $^1\text{O}_2$ and their exceptional ability of releasing it upon controlled cycloreversion⁵. The synthesis has been achieved after optimization of published procedures. We started to study photooxygenation conditions with 9,10-diphenylanthracene (DPA) as reference compound and the obtained product was fully characterized by NMR, IR and UV-Vis spectroscopies and ESI-MS spectrometry. In parallel, we successfully entrapped Ce6 in the CyD-based NPs with a binding constant of 10^3 M^{-1} without affecting its ability to generate $^1\text{O}_2$ in deuterated buffer solution. At the moment, we are optimizing the photooxygenation procedures for the synthesized derivatives as well as their encapsulation in the polymeric carrier together with Ce6. Upon co-encapsulation molecular oxygen release will be evaluated.



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Synthesis and characterization of a NIR sensitizer and its encapsulation in polymer nanoparticles

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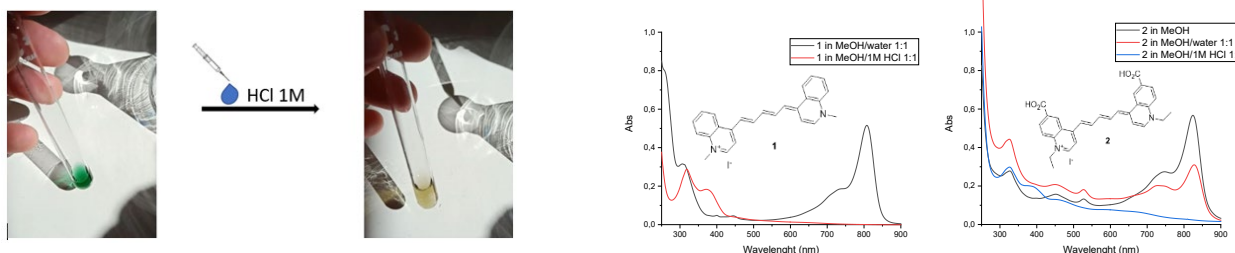
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NIR fluorescence offers considerable advantages in biological applications, due to the negligible background signal, the minimal tissue damage and a high depth of tissue penetration. Indeed, scattering and auto fluorescence represent two important effects in living organism.[1]

Polymethine dyes are a class of NIR fluorophores, characterized by outstanding optical properties, such as high molar extinction coefficients and tunable absorption wavelengths, which have been extensively employed in different research areas, including chemistry and biology. The photophysical and photochemical properties are determined by the presence of a flexible polymethine chain and the nature of the end groups. Among heterocyclic moieties, quinoline is recognized as an attractive scaffold for the development of new fluorescent reagents, because of its small molecular size and its ability to interact through hydrogen bonds, due to the presence of the heterocyclic nitrogen atom. Several quinoline derivatives have been isolated from natural sources and possess significant bioactivity, so they have been widely used in medicinal and industrial chemistry.[2] In the literature, there is very little information concerning polymethine dyes bearing quinoline moieties and, more particularly, those obtained from quaternary salts of lepidine (namely 4-methylquinoline).

Herein, the full characterization of a model pentamethine cyanine dyes and a thorough investigation of the chemo- and photostability of lepidine-based cyanines is presented, so as to describe their potential and limitations, which is food for thought to study how to improve their applicability. In order to increase the stability and biocompatibility of these systems, one of the synthesized cyanines has been encapsulated in polymeric nanoparticles of Pluronic F-127, that in recent years represents one of the most attractive drug carriers in terms of size and architecture.



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Near-Infrared Fluorescence Dye-Loaded Polymeric nano particle: PLGA

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Strong absorbance on NIR and excellent photochemical properties of polymethine dyes make them excellent probe in the theranostics application. Even if squaraines and cyanines are characterized by high molar absorption coefficients, remarkable brightness, fluorescence and photostability in organic media [1], poor chemical and aqueous solubility, medium cytotoxicity, and short blood circulation half-life in physiological conditions limits their wide application [2]. In this context, the incorporation of these dyes inside multi-functional nanoparticles (NPs) is extremely important to prevent the formation of dye aggregates in aqueous environment and protect the photophysical characteristics.

Poly(lactide-co-glycolide) (PLGA) has attracted considerable attention due to its physicochemical properties: biodegradability and biocompatibility, FDA and EMA approval in drug delivery systems for parenteral administration, well described versatile formulations and methods of production adapted to various types of hydrophilic or hydrophobic molecules, possibility of sustained release, and versatility in functionalization to target nanoparticles to specific organs or cells.

The present work deals with the design of PLGA NPs for the incorporation of several polymethine dyes with different structural features. NPs-dye complexes have been characterized by means of NTA, SEM, UV-Vis and fluorescence spectroscopy. They exhibit excellent optical properties and remarkable photostability.

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