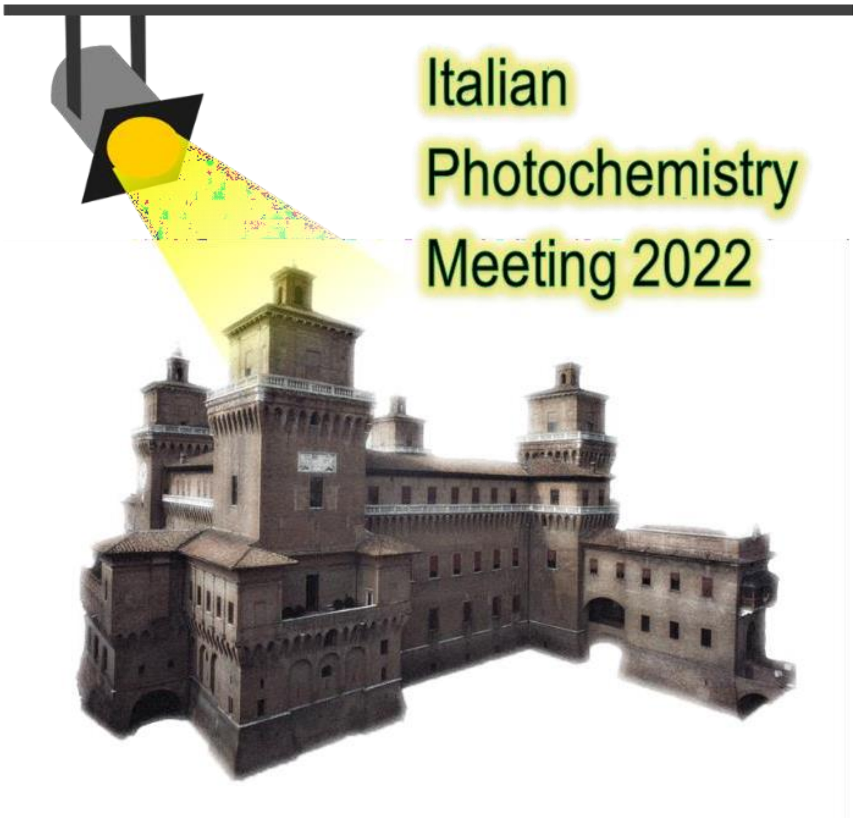
BOOK OF ABSTRACTS



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Plenary-PL1

Hybrid Molecular Anodes for Sustainable Energy Applications

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The replacement of fossil fuels by a clean and renewable energy source is one of the most urgent and challenging issues our society is facing today, which is why intense research is devoted to this topic recently. Nature has been using sunlight as the primary energy input to oxidize water and generate carbohydrates (a solar fuel) for over a billion years. Inspired, but not constrained by nature, artificial systems [1] can be designed to capture light and oxidize water and reduce protons or other organic compounds to generate useful chemical fuels. In this context this contribution will present how molecular water oxidation catalysts can be anchored on solid supports to generate powerful hybrid electro- and photo-anodes for water splitting [2].

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Plenary-PL2

Self-assembly of luminescent metal complexes in solution and *in vivo*

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Luminescent molecules that can undergo self-assembly are of great interest for the development of new materials, sensors, biolabels…. In some cases the assembly can lead to an enhancement of the emission, a change in the luminescence energy and even to unexpected biological phenomena.

The talk will illustrate some of the recent results on the self-assembly of platinum complexes and their evolution in solution[1]. The different species that evolve from the initial assembly can be visualize thanks to their different photophysical properties and the control of the solvents determines the kinetics of their evolutions. The stabilization of transient species, formed in the assembly process can be achieved using cage type structures can lead to their stabilization or even existence in solution, in a condition out of equilibrium. We recently demonstrated[2] that it is possible to entrap intermediate states of luminescent assemblies and prevent their thermodynamic evolution towards the equilibrium state. Furthermore the use of nanocages able to break on demand allows the transport and release in cells of such species and therefore their dynamics can be observed in living cells.

Finally some water soluble compounds where studied to follow the self-assembly *in vivo* and the resulting reactivity/toxicity of such species. We employed transparent polyps, *Hydra vulgaris* to study the self-assembly in living animals that can be monitored by the appearance of an intense green/yellow emission. Interestingly, differences in the fluorescence emissions were observed in tentacle and body regions. Also morphological or behavioural alterations where followed to understand dose dependent toxicity when the *Hydra* were treated with different doses of Pt(II) complex.

An extraordinary phenomenon was detected with one of the complex that showed a clear effect on pluripotent stem cell proliferation, especially at low doses. This effect was further demonstrated by the increased number of differentiated cells, i.e. neurons and gland cells and it is still under study.

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Plenary-PL3

Real-time observation of conical intersection in biomolecules

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Conical intersections (CIs) are regions of the potential energy landscape of a molecule where the electronic and nuclear degrees of freedom become strongly mixed and the Born–Oppenheimer approximation breaks down. CIs are ubiquitous features in the photophysics and photochemistry of molecules and can be considered as “doorways” through which the photoexcited wavepacket is efficiently funneled to a lower-energy electronic state. CIs play a dual role in the interaction of biomolecules with light: either to promote efficient conversion from a reactant to a product state in a photochemical reaction or to enable efficient dissipation of excess electronic energy, preventing a potentially harmful photochemical reaction [1]. An example of the first case are visual opsin proteins, in which the photoexcited retinal chromophore exploits a CI to promote ultrafast photoisomerization to a ground-state photoproduct which triggers visual transduction. An example of the second case are nucleobases, the building blocks of DNA, for which CIs are used to promote rapid dissipation of excited state energy, preventing photoreactions which could damage the genetic code.

Given the extreme speed of the processes leading to CIs, ultrafast optical spectroscopy is the elective tool for their observation. However, the direct visualization of a wavepacket passing through a CI is challenging, because the energy gap between the interacting levels changes very rapidly over a short time, calling for the combination of high temporal resolution and broad spectral coverage. In this talk I will present examples of real-time visualization of CIs in biomolecules (opsin proteins [2] and nucleobases [3, 4]) using a specially developed ultrafast transient absorption spectroscopy system combining sub-20-fs time resolution with broad frequency tunability, from the UV to the infrared [5]. I will also discuss the potential of X-ray free-electron lasers to open new spectroscopic windows for the detailed study of the CI dynamics, via element-specific probing of ultrafast electronic and structural dynamics.

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Plenary-PL4

Supramolecular Photosystems derived from Ferrari Red

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Research on dye molecules has been continuing to be at the forefront of new developments in chemistry owing to the versatile functional properties associated with π-conjugation. On a supramolecular level, appropriately controlled spatial arrangement of dyes enables pivotal functions, the most intriguing examples being provided by the light-harvesting systems of plants and photosynthetic bacteria which contain a large number of chlorophyll and carotene chromophores organized in specific arrangements by intra- and intermolecular interactions. Inspired by this natural blueprint, the field of supramolecular photochemistry has been established.[1]

During the last years, we have intensively investigated the organization of various functional dyes, e.g. perylene bisimides, merocyanines, diketopyrrolopyrroles and squaraines, by non-covalent forces into desirable nanoscale architectures as well as liquid-crystalline and crystalline solid state materials[2] which nurtured successful research in organic electronics and photovoltaics.[3] In this lecture, I will provide an overview on our achievements in the preparation of multichromophoric architectures based on perylene bisimides by folding and self-assembly strategies and elucidate structure-property relationships with regard to exciton coupling, symmetry-breaking charge separation and singlet fission processes as required for the efficient harvesting and conversion of sun light.[4,5]

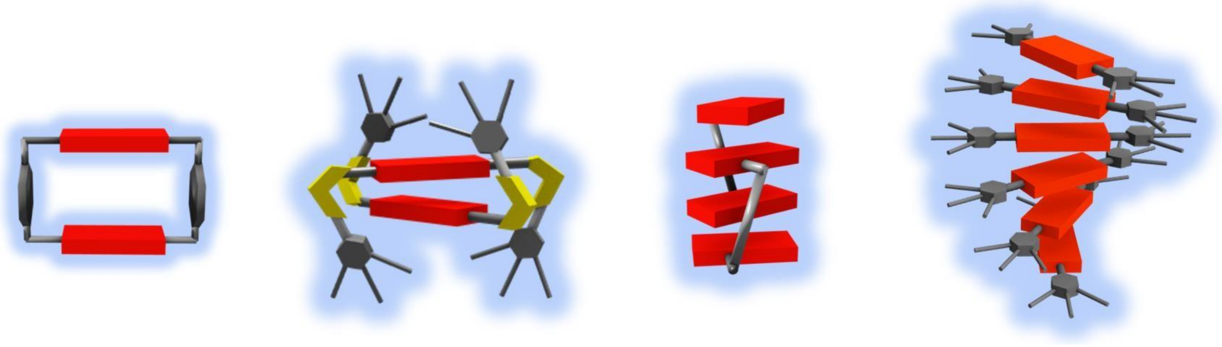

Fig. 1. Examples for supramolecular structures utilized for photophysical studies.

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Keynote-K1

Innovative and Sustainable Materials for Emerging Photovoltaics: From Panchromatic to Colourless

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Emerging PhotoVoltaic (e.g. Dye-Sensitized Solar Cells, DSSCs, and Perovskite Solar Cells, PSCs) has gained an increasing attention as low-cost and sustainable alternative to conventional silicon-based PV. On one hand, DSSCs[1] have been thoroughly investigated in the last three decades due to their numerous advantages, such as cheap and simple preparation methods[2], the possibility of being integrated in buildings and astonishing performances under indoor and diffuse illumination conditions (□ = 33%).[3] On the other hand, PSCs) are the breakthrough among emerging PV technologies coupling very high efficiency (comparable to Si-based devices) with relatively low costs. Unfortunately, long-term stability of PSCs is the main issue to be solved for a forthcoming commercialization. The stability of PSCs mainly suffers for water and oxygen infiltration as well as prolonged exposition to UV radiation.

Commercially available PV devices are usually panchromatic, a valuable feature to exploit a major part of the solar radiation, yet this will exclude PV from being applicable is specific application (*i.e.* building integrated, agrivoltaic, and automotive). Therefore, it would be very interesting to develop tailored materials to be exploited in specific application.

In this award contribution, some of the most interesting approaches and materials development in the research group I am and I was involved will be presented. From the quest of panchromatic sensitizers and/or tandem-DSSC[4] devices aiming at fruitfully utilize all the visible spectrum, the attention was shifted to nearly colourless devices exploiting the NIR portion of the solar spectrum[5]. Such a new conception devices have been integrated in semi-transparent mechanical stacked DSSC/PSC tandem devices, with the latter mainly absorbing UV radiation, reaching photoconversion efficiency close to 10% with a maximum Light Utilization Efficiency of 3.5%. This really promising result has been obtained taking advantages of the utilization of a highly transparent polyurethane-based thermosetting resin playing the double role of gluing agent and refractive index matcher.

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Keynote-K2

Mechanistic Investigation Of The Molecular Movement Of Photochemical Actuators

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Photochemically driven molecular switches and unidirectional molecular motors represent a fascinating fundamental research topic.[1,2] These *photoactuators* can drive the dynamics of molecular systems and devices at the nanoscale, a peculiar feature that has found applications in smart materials and biomedical sciences. Classic photoactuators like azobenzene or the Feringa molecular motor have been known for decades, and since then, significant advances in their respective designs have been achieved. However, the quest to synthesize molecules tuned for a specific task requires a deep understanding of their motion

This talk will focus on selected examples of the application of the toolboxes offered by organic synthesis, spectroscopy, computational chemistry and physical organic chemistry to predict, construct and investigate novel photochemically driven switches and motors (Fig. 1).[3,4] This approach allows the understanding of the behaviour of new structures and discovering of the mechanisms underlying their movement at the molecular scale.

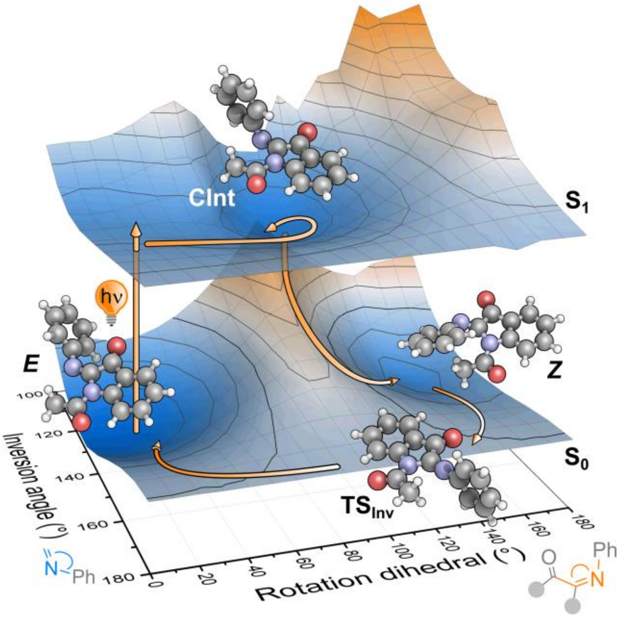

Fig. 1. Ground and excited state isomerization pathways of the phenylimino indolinone photoswitch.[3]

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Keynote-K3

Photon upconversion based on triplet-triplet annihilation processes in smart media to enhance the recovery of incoherent radiation

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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 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] i.e. in photovoltaic cells, for solar fuel production, in photocatalysis and photopolymerization, in photonic science, and for bio-imaging *in vivo* conditions. In this work, the TTA-UC is studied in smart media, addressing two different aspects that hamper the diffusion of commercial TTA-UC devices. Firstly, the sustainability of solvents used to dissolve the chromophores pair has been taken into account. Traditional solvents include toluene and chlorinated-benzenes, for example, that are toxic and dangerous for the environment and produce big amount of special waste. Therefore, the TTA-UC among platinum(II)-2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin (PtOEP) and 1,3,6,8-tetraphenylpyrene (TPPy) has been studied in unconventional green solvents. [3]

With the aim to protect the UC-couple and overcome the quenching effect of oxygen on the involved excited states, the second part of the work is focused on the preparation of solid-like materials able to compartmentalize a benchmark UC-couple (PtOEP and 9,10-diphenylanthracene, DPA).[4] Furthermore, the experimental conditions have been controlled to generate the upconverted signal in air-equilibrated environments, using an incoherent light source to excite the samples. Oil-in-silica capsules have been synthetized and fully characterized from an optical and a morphological point of view. For the purpose of increasing the protection from bimolecular oxygen, TTA-UC capsules are included in poly(vinyl alcohol) (PVA) polymer films. Similar synthetic strategy has been also used with different fatty acids. In particular, oleic acid and elaidic acid, two geometric isomers behaving like phase-changing materials,[5] are used to evaluate the effect of temperature in TTA-UC mechanism. The solidness of the prepared capsules has been tested in the presence of aggressive reagents involved in periodic reactions.[4] The stability of the capsules enables to set conditions to achieve intensity modulation of UC-emission, in order to develop a chemical system behaving like a demultiplexer. Moreover, optical communication experiments, between the upconversion pair and N-octylacridinium perchlorate, monitored with fluorimetric techniques have been successfully achieved.

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Keynote-K4

Iron Sensitized Solar Cells (FeSSCs)

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Due to the strong increase in the world energy consumption, and need of exploiting carbon neutral energy sources, increasing efforts by the scientific community have been devoted to the exploitation of solar energy with sustainable and low impact technology. In recent years, the silicon photovoltaic market has been rapidly growing. Dye Sensitized Solar Cells (DSSC) could complement the established silicon technology as white light energy harvesters with unique properties such as transparency, low cost, capability to work under diffuse light and ample palette of available colors, suitable for indoor and outdoor architectonic integration. Should be interesting to employ sensitizers characterized by abundant and non-toxic elements, such as the first-row d block elements; among this series iron exhibits the best natural availability. 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. In a first contribution, our group has tried to rationalize the charge transfer dynamics of **C1,** a homoleptic complex bearing σ-donating NHCs and π-accepting carboxylic groups as anchoring moieties, which initially reported rather low performances (0.13 % of PCE%), reaching 1% of PCE% [1]. We have moved the attention to heteroleptic Fe(II)NHC complexes with the aim to increase the excited state directionality, this led to a power conversion efficiency of 1.5% in the case of **ARM13**, the asymmetric analog of our standard **C1** [2]. We 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. With **ARM130**, by exploiting an optimized electrolyte and TiO_2 photoanode, we have obtained 1.83% of efficiency [3]. In our last contribution, we have realized a series of two new Fe(II)NHC sensitizers bearing thienylcyanoacrylic anchoring groups (ThCA) with the aim to enhance the metal to surface charge separation and the light harvesting capability in iron-sensitized DSCCs (FeSSCs). In these new Fe(II) dyes, the introduction of the ThCA moiety remarkably extended the spectral response and the photocurrent by comparison with the carboxylic analogues. The co-sensitization based on a cocktail mixing a carboxylic and a ThCA-iron complex (**C1** and **ARM12**) produced a panchromatic absorption, up to 800 nm and the best photocurrent and efficiency (Jsc: 9 $mAcm^2$, PCE: 2%) ever reported for a FeSSC.

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Oral-O1

$CuInS_2$ quantum dots as photoanodic material in photoelectrochemical cells

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Copper Indium Sulfide Quantum dots (CIS QDs) are valid alternatives to conventional quantum dots for their non-toxicity, elevated molar absorption coefficients over the entire visible spectrum and prolonged emission lifetimes, that make them promising materials as sensitizers for photoanodes in photoelectrochemical cells (PEC).

Acid-functionalized CIS QDs are known to adsorb over and sensitize TiO_2-FTO electrodes. The photocurrent density, upon solar irradiation, can be ameliorated by passivating the deposited CIS QDs with a CdS shell.

The currently adopted synthesis of CIS QDs for photoanodes are not efficient or don't adsorb properly onto TiO_2. Here, we propose a facile and versatile synthesis of lipoic acid-functionalized CIS@CdS QDs that display elevated photocurrent densities (≈ 7 mA cm^{-2}) when deposited onto TiO_2-FTO photoanodes, using a Pt wire as counter electrode, under simulated AM 1.5 G solar irradiation. Current research is focused on the photo-oxidation of biomasses and water.

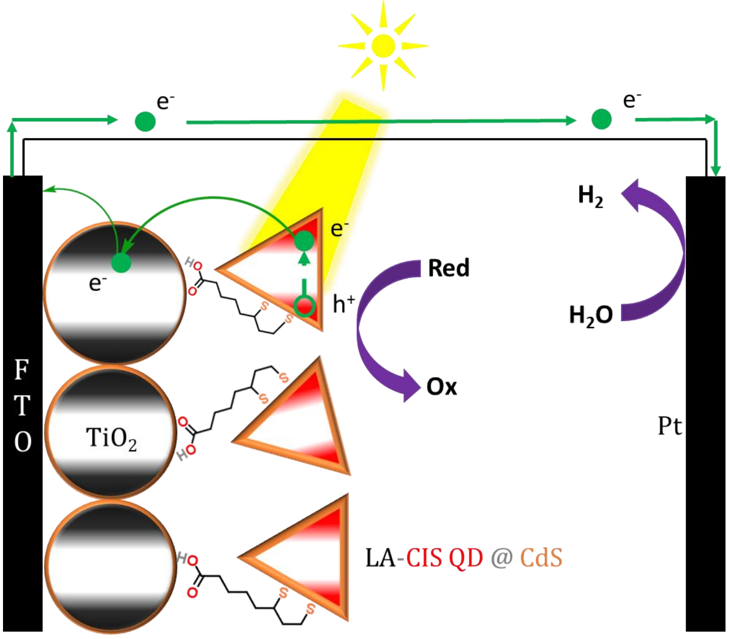

Fig. 1. Working principle of a Lipoic Acid-functionalized CIS QDs-sensitized PEC under solar irradiation

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Oral-O2

Photocatalytic Water Oxidation at the Lipid Bilayer−Water Interface: a Mechanistic Study

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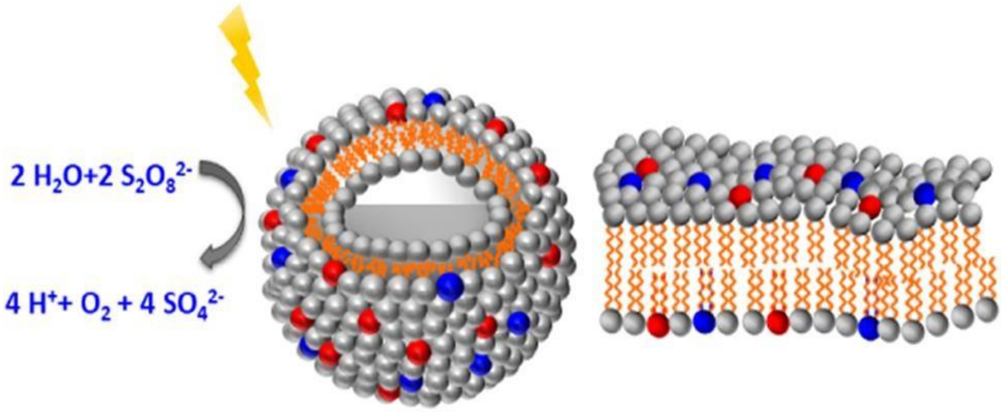
In nature, water oxidation takes place in photosystem II which is assembled within the thylakoid membranes in chloroplasts.[1,2]

Photocatalytic water oxidation in liposomes using an amphiphilic ruthenium(II)-trisbipyridine photosensitizer and an amphiphilic 6,6'-dicarboxylato-2,2'-bipyridine-ruthenium(II) catalyst with a water soluble sacrificial electron acceptor forms a much simpler system, but the effect of embedding a photocatalytic system in liposome membranes on the mechanism of photocatalytic water oxidation was not well understood. Several productive and unproductive pathways have been identified by steady-state and time-resolved spectroscopy, which give quite different results from those of the corresponding homogeneous system.[3] Overall, understanding and comparing these phenomena explains why photocatalytic water oxidation is limited by different factors in homogeneous and liposomal systems, and allows rational optimization that might be of general importance for light-driven catalysis within self-assembled lipid interfaces.



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Oral-O3

Cross-linking Perylenebisimide “Quantasomes” with PEG chains to template hydration shells and enhance oxygenic photosynthesis

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Nature is an excellent source of inspiration for the design of solar water splitting photosystems, such as the emerging class of artificial quantasomes: multichromophore architectures integrated with catalytic cores that convert radiation quanta into chemical energy by mimicking the PSII oxygenic function.[1] Specifically, the way PSII paired function is regulated by protein - protein interactions, that hold together the membrane stacks while favoring the PSII contact and consequently illumination adaptation, could be implemented in novel artificial quantasomes to boost performances and stability.[2] This asset brought us to cross-link the quantasome network by installing, using click-chemistry, different hydrophilic azido-polyethylene glycol (PEG) bridges between the propyl terminated perylene bisimides units surrounding the catalytic center (Ru_4POM).[3] Here, it will be illustrated how this locking strategy delivered Quantasomes (QSn-Lock) with controlled growth and increased water interaction, resulting in improved oxygenic photocatalysis compared to first-generation QS as demonstrated by chopped light linear sweep voltammetry, chronoamperometry, light management and incident photon to current efficiency.

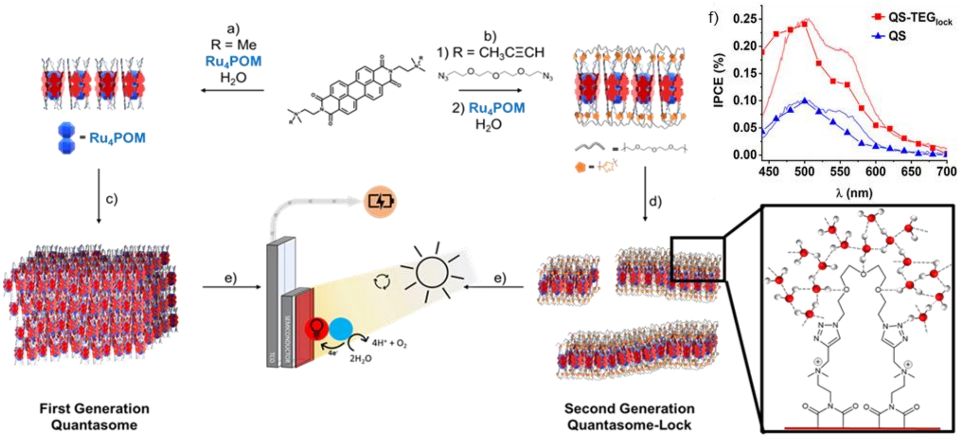

Fig. 1. Synthetic plan for the assembly of artificial quantasomes a) self-assembly of bis-cationic perylene bisimides with Ru_4POM in water b) self-assembly of biscationic perylene bisimides after installation of a clickable 2-propynyl terminals to cross-link the QS networks with hydrophilic polyethylene glycol (PEG) connectors. c) and d) lateral and hierarchical aggregation of QSs into nano-lamellae. e) immobilization of the QS on state-of-the-art photoanodes to screen the oxygenic performance f) corresponding action spectra with superimposed diffuse reflectance spectra.

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Oral-O4

Implementation of copper tungstate-based photoanodes for solar energy conversion

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Solar water splitting in a photoelectrochemical (PEC) tandem cell is a leading candidate reaction to convert and store solar energy in high-value chemicals that could replace fossil sources, such as green hydrogen [1]. Identifying light-absorbing materials that satisfy the requirements of stability and performance is a very current issue, especially when employing them as photoanodes in the demanding water oxidation reaction. In this frame $CuWO_4$ (band gap = 2.3 eV) has recently gained increasing interest [2], although its efficient use is limited by a severe and undesired internal charge recombination [3].

In this work, this crucial issue of $CuWO_4$ photoanodes is addressed by adopting a partial Mo^{6+} for W^{6+} substitution strategy resulting in $CuW_{1-x}Mo_xO_4$ electrodes with a greatly enhanced visible light-induced photoactivity compared to pure $CuWO_4$. We thus systematically optimized both the film thickness in the wide 250-700 nm range and the Mo^{6+} for W^{6+} substitution degree (10-80%), by adopting an aqueous-based deposition procedure onto fluorine-doped tin oxide (FTO) glass substrates. A thorough PEC investigation under simulated solar light irradiation, either in pure water oxidation or in the presence of $NaNO_2$ as suitable electron donor species [4], led to the identification of the *ca.* 250 nm thick $CuW_{0.5}Mo_{0.5}O_4$ film with a 1:1 W:Mo molar ratio as the best performing electrode, ensuring an optimized compromise between light absorption and photogenerated charge carriers separation. Furthermore, with the aim to further boost the charge carrier separation within the photoanodes, the best performing $CuW_{0.5}Mo_{0.5}O_4$ films were combined either in a heterojunction with $BiVO_4$ or in a double heterojunction with both WO_3 and $BiVO_4$. Incident photon to current efficiency (IPCE) analyses at the thermodynamic water oxidation potential of 1.23 V vs. RHE demonstrated the definitely superior performance of both $CuW_{0.5}Mo_{0.5}O_4/BiVO_4$ and $WO_3/CuW_{0.5}Mo_{0.5}O_4/BiVO_4$ coupled systems compared to the individual components, over the entire investigated spectral range (Figure 1).

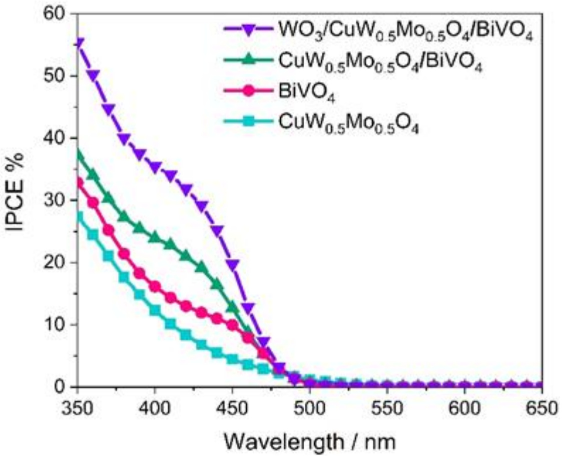

Fig. 1. Incident photon to current efficiency (IPCE) of different photoanodes at 1.23 V vs. RHE in 0.1 M K_3BO_3 electrolyte solution (pH = 9) under front-side irradiation.

In particular, the photoactivity was found to be maximized under selective excitation of a sufficiently thick $BiVO_4$ overlayer, allowing to minimize the competitive electron-hole recombination path occurring instead under simultaneous excitation of the three oxides by irradiation through the FTO back-side.

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Oral-O5

Pulsed Laser deposition methods for sustainable inorganic photoactive nanomaterials

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Water oxidation represents the anodic reaction in most of the photoelectrosynthetic setups for artificial photosynthesis developed so far. The efficiency of the overall process strongly depends on the joint exploitation of good absorber domains and interfaces with minimized recombination pathways. A key design principle for composite photoelectrodes performing these functions is the formation of an adaptive junction, which dictates the kinetics of both hole transfer and charge recombination. [1] To this aim, control over morphology of the materials involved in the composite formation is critical, since adaptive junctions requires porosity, while dense and electrolyte impermeable layers hinder the pivotal charge compensation processes at the interface.

We report here on the effective coupling of a thin-layer hematite absorber with amorphous porous nickel−iron oxide catalysts prepared via pulsed laser deposition, showcasing the unparalleled versatility [2] of this fabrication technique, which allows tuning of a wide range of key materials properties. Electrochemical impedance spectroscopy is employed to investigate the mechanisms of photocurrent generation, and the direct comparison with all-iron and all-nickel catalytic counterparts highlights the role of the adaptive junction.[3] The design principles demonstrated here open the way to high-performance components based on materials which are both economically and environmentally sustainable.

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Oral-O6

New Photocatalyst for the Degradation of NSAIDs

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Water is the crucial element for life on Earth, but the availability of fresh water is decreasing. One of the main concerns for the reuse of urban wastewater is the presence of non-negligible quantities of pharmaceutical compounds [1]. Among pharmaceutical compounds, non-steroidal anti-inflammatory drugs (NSAIDs) are the most frequently revealed drugs in the environment as they are also some of the most widely used [2]. Here, we propose a new composite photocatalyst to be used for the degradation under uncoherent visible light of two of most common NSAIDs, Ketoprofen (KTP) and Diclofenac (DCF). The photocatalyst is based on a MOF, namely F4-MIL-140(Ce), loaded with controlled amounts of iron oxide (Fe_3O_4) nanomaterials. We tested the photocatalytic activity of the material in water solutions of the aforementioned NSAIDs and we determined the kinetic of the degradation. It is the first time such material was prepared and used for photocatalysis and, from our studies, it displays good features for the degradation of NSAIDs. In addition, it is also easy to recover after use as it can be separated from water by simply apply a magnetic field.

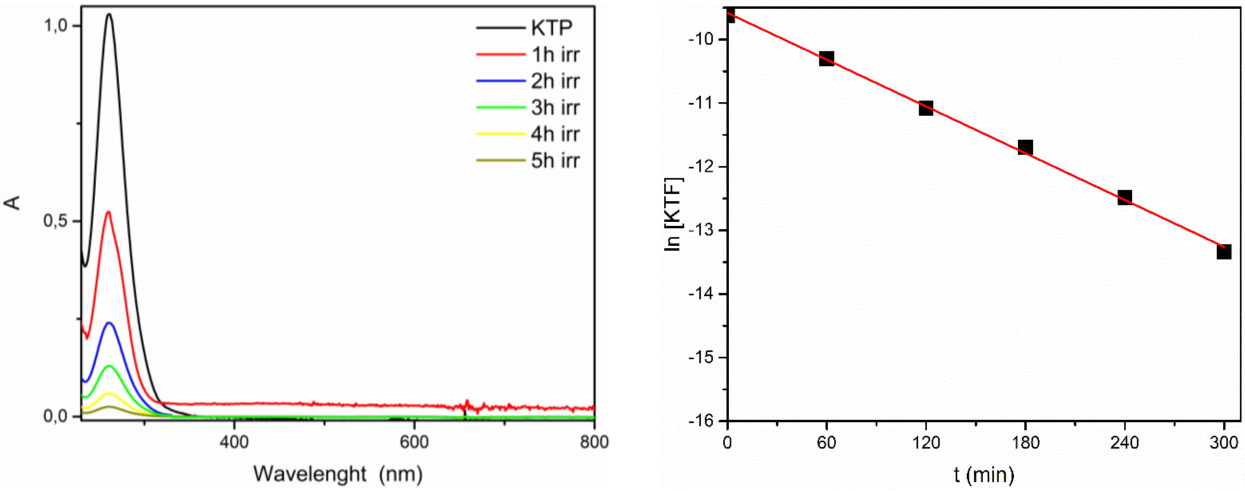

Fig. 1. Examples of photodegradation experiments, UV-Vis analyses at different irradiation time on the left, fitting of the calculated concentration through first order law on the right.

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Oral-O7

Nanoengineered photoresponsive vesicles

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The construction of supramolecular architectures able to respond to external stimuli has attracted an increasing amount of attention due to their potential application in nanotechnology.[1] Particular relevance has been given to the design of photoresponsive devices, as the use of light as an external stimulus allows them to function in a clean and time- and space-controlled way.[2] We report the study of liposomal vesicles functionalized with a class of thread-like molecules comprising a photoactive azobenzene unit enclosed within two amphiphilic terminals. Upon intercalation in the bilayer membrane, such compounds proved able to highly influence the supramolecular interactions between the functionalized vesicles. Specifically, the doped liposomes displayed a reversible and non-destructive aggregation-disaggregation behaviour which can be regulated by light energy input. Importantly, achieving macroscopic outputs through molecular scale engineering can be of great interest in nanomedicine as liposomes are widely used as model systems of natural cell membrane.[3]

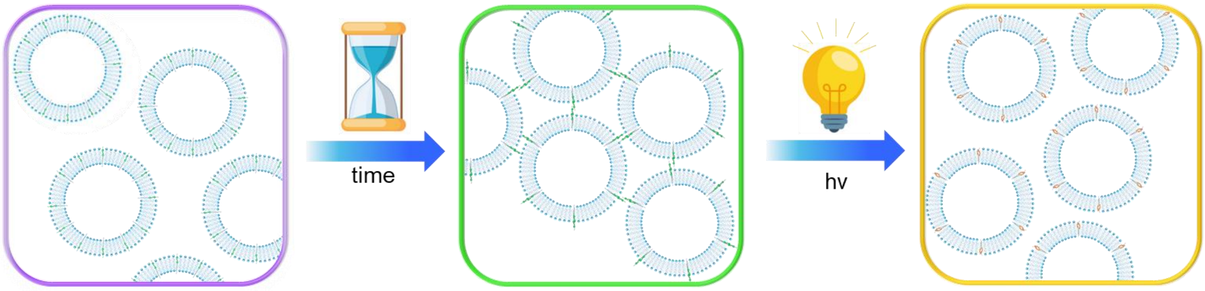

Fig 1. Schematic representation of the photoresponsive vesicles behaviour.

Acknowledgements

Financial support from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no. 692981) is gratefully acknowledged.

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Oral-O8

Operating a molecular pump with light and chemical fuel pulses

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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. [1] Light-driven artificial molecular pumps have recently been realized in our laboratory based on the self-assembly between a crown ether macrocycle (**1**) and a linear component (*E*-**2**H^+) consisting of a photoswitchable azobenzene unit and a dibenzylammonium unit, which is a recognition site for the ring. [2,3] Their operation relies on the light-induced modulation of the kinetics of self-assembly and of the stability of the complex *via* an energy ratchet mechanism. In order to increase the efficiency of the pump, a larger destabilization of the complex is required. Towards this goal, the use of a combination of light and chemical fuel pulses was envisaged.[4] The operation cycle starts from the neutral amine *E*-**2**, that is activated towards complexation with **1** by protonation with an acid fuel. Since the kinetic barrier to threading on the azobenzene side is lower than on the pseudostopper side, threading of **1** occurs preferentially from the azobenzene side. Subsequently, the light-induced *E/Z* isomerization of the azobenzene unit leads to an increase of the dethreading kinetic barrier above that of the pseudostopper. Finally, the spontaneous decarboxylation of the carboxylic acid, to form a carbanion, is expected to abstract the proton from the ammonium station promoting decomplexation through slippage of **1** over the pseudostopper. Overall, through this sequence of stimuli, a directional transit of the ring from the azobenzene to the pseudostopper side is achieved (Figure 1). Interestingly, the direction of the relative motion of the ring and axle moieties can be reversed by reversing the sequence of fuel and light stimuli. Finally, the use of a photocaged carboxylic acid fuel is envisaged in order to operate the pump autonomously.[5]

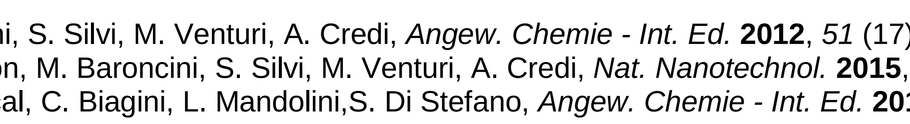

Fig. 1: operation of the light-driven supramolecular pump with light and fuel pulses

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Oral-O9

Development of high-sensitive electrochemiluminescent-based sensor for the detection of Sars-CoV-2 virus

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The recent pandemic outbreak clearly highlighted the importance of a fast, efficient and cheap detection of viruses – and other pathogens – to prevent their spread. The most sensitive methods commercialized are based on techniques that amplify the viral RNA through highly selective but expensive and time consuming polymerase chain reaction (PCR).

As recently proven[1], an efficient alternative to PCR can be found combining Surface Cooperative Hybridization technology with electrochemi-luminescence (ECL).

ECL is a versatile transduction mechanism ensuring high sensitivity and very low background noise. In this work we exploited the ECL signal obtained from $[Ru(phen)_2(DPPZ)]^{2+}$ intercalated into double strand nucleic acid formed upon hybridization of single strand Sars-CoV-2 RNA with single strand thiolated oligo DNA probes anchored to the electrode surface.

The optimization of this novel detection platform and the exploitation of fast and simple thermal extraction of the viral nucleic acid allowed us not only to overcome the time-consuming purification and analysis of the PCR technique, but also to obtain a sensing platform for the detection of Sars-CoV-2 RNA, also in real samples, with even lower limit of detection (LoD = 140 copies · mL^{-1}) compared to the gold-standard PCR.

The results herein presented help to pave the way to realize simple, portable, cheap and reliable devices to detect several pathogens, in Point-of-Care (PoC) format.

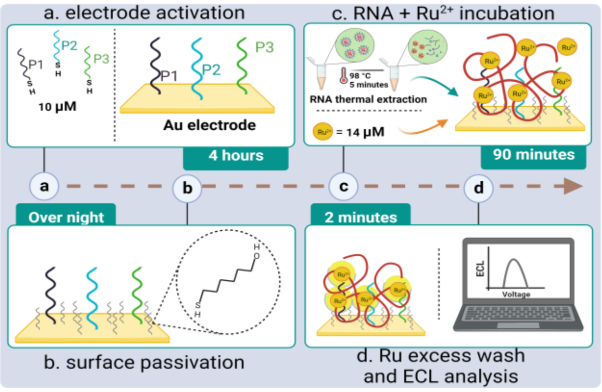

Fig. 1. Schematic protocol of the PCR-free detection strategy: (a) Immobilization of specific probes P1, P2 and P3 and of (b) 6-Mercapto-1-hexanol on the surface of a gold electrode; (c) recognition of Sars-CoV-2 RNA by surface cooperative hybridization and intercalation of $[Ru(phen)_2dppz]^{2+}$; (d) wash of excess of Ruthenium and Sars-CoV-2 genome detection through ECL analysis.

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Oral-O10

A Multiwavelength Photoreactor for Batch and Flow Chemistry – Development and Applications

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Photochemistry, especially the well-documented Minisci reaction offers a particularly useful approach to create new C(sp^2)-C(sp^3) bonds, however, traditional batch procedures often require long reaction times (27-44 hours).[1-4]
Continuous flow technology enables the acceleration of the reaction, furthermore, multiple synthetic steps can be merged into one sequence with careful planning, resulting in higher yields.[5]
Considering such benefits, our aim was to decrease the reaction times and increase the yield of a two-step synthetic process, including the formation of a N-(acyloxy) phthalimide (NAP) intermediate and a Minisci reaction starting from lepidine (4-methylquinoline, Figure 1.).

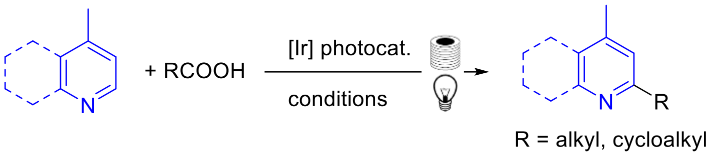

Fig. 1 Photocatalytic Minisci reaction

Further case studies will be presented on photoinduced benzylic bromination and dual catalytic decarboxylative C-C coupling.
The photocatalytic experiments were performed with the PhotoCube™, a multifunctional photoreactor for batch and flow applications with 7 simultaneously available wavelengths (365, 395, 457, 500, 523, 595, 623 nm) and white light. Light intensity can be regulated for each wavelength independently and/or simultaneously, which provides opportunity for reactions requiring multi-wavelength irradiation or multi-step applications.[5]

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Oral-O11

Incorporation of donor-acceptor Stenhouse adducts in liposomes and stimuli-induced guest relocation

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Donor-Acceptor Stenhouse Adducts (DASAs) are a new class of photochromic systems that isomerize upon visible light stimulation from a colored, hydrophobic open form to a colorless, zwitterionic closed form.[1] The significant change of the physicochemical properties, including polarity, associated with the switching process makes DASAs attractive candidates for use as actuators in lipid membranes.[2] DASA derivatives with different alkylamine donors (figure 1a) have been investigated and intercalation within the bilayer membrane of POPC liposomes has been explored. The functionalized liposomes were studied by dynamic light scattering and UV-vis spectroscopy, allowing to determine the encapsulation efficacy of each guest and the effect of the intercalation on the diameter of the vesicles. In all cases, a spontaneous interconversion of the open form to the cyclized form was observed over time, which could be accelerated by visible light irradiation. The subsequent partitioning of the cyclized species was studied via size-exclusion chromatography, showing it is possible to obtain guest relocation from the membrane of the liposomes to the aqueous environment upon isomerization (figure 1b).

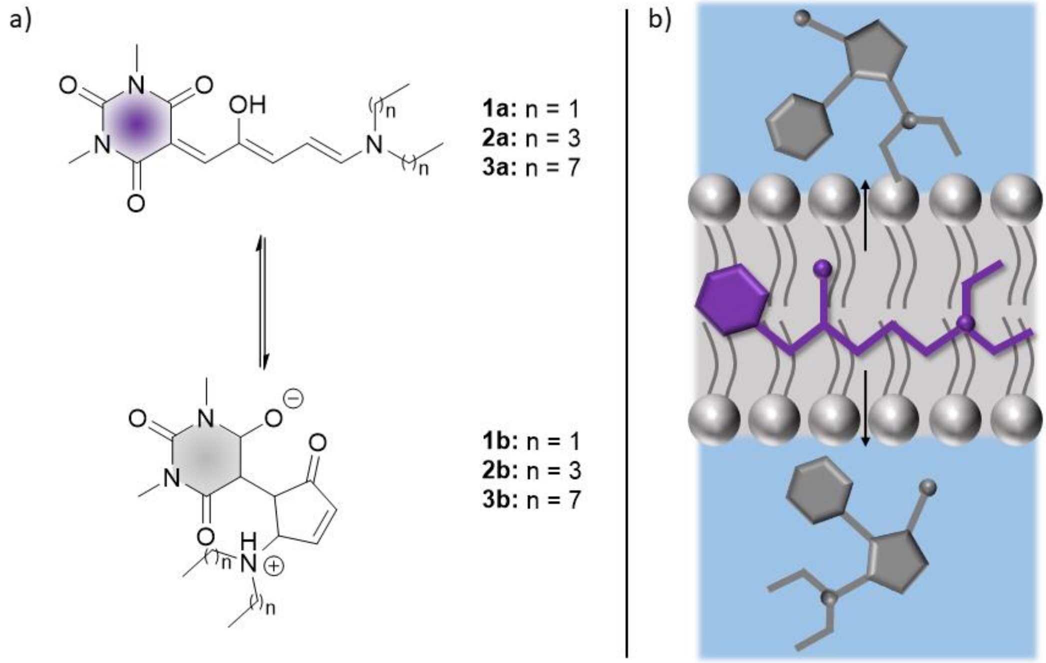

Fig. 1. a) structures of the DASAs employed; b) schematics of DASAs relocation upon isomerization.

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

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Oral-O12

A green photothermal material for light-controlled artworks restoration

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Artworks vandalism is a very common issue and removal of unwanted paint layers is a big challenge in restoration[1]. Indeed, spray paints are usually difficult to be eliminated and it is also necessary to act with high precision, without modifying the original parts of the artwork[2]. Here we report a new method to remove a typical spray varnish (alkyd resin), exploiting photothermal effect. The technique consists of depositing an electrospun mat, wet by a proper solvent for the varnish, on the surface and favouring alkyd layer removal by a light stimulus. This is possible by embedding melanin, widely known for its photothermal properties[3], in the electrospun mat and irradiating the system with red light: the temperature increase triggers the solvent release from the mat fibers to the surface and also increases alkyd resin solubility, leading to its swelling (Fig. 1). Compared to other removal techniques, the combination between the use of electrospun mats and a photothermal material allows to have high control on the solvent release, preventing artwork damage. Moreover, by using a green solvent (γ-Valerolactone), mat fibers made up of a natural polymer electrospun in water and squid ink as a melanin source, we can obtain a totally eco-compatible system. This method represents a novel interesting application of the photothermal effect and its fastness, ease and safety make it already suitable to be used in the artwork restoration field.

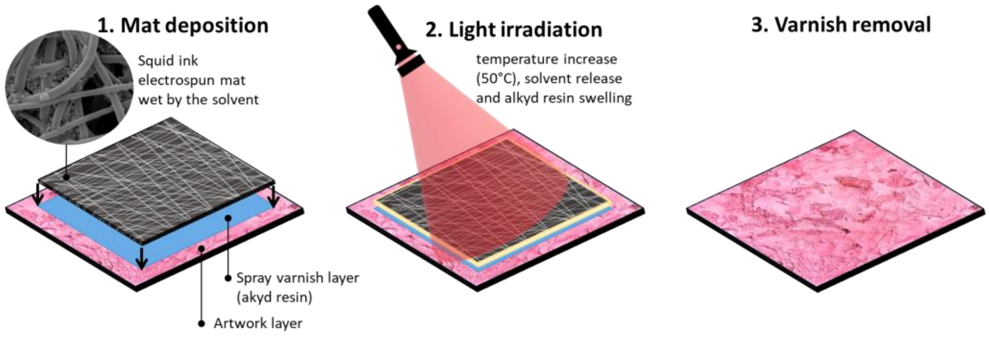

Fig. 1. Photo-induced varnish removal process by means of photothermal electrospun mat

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Oral-O13

New luminescent organic nanomaterial for sensing applications

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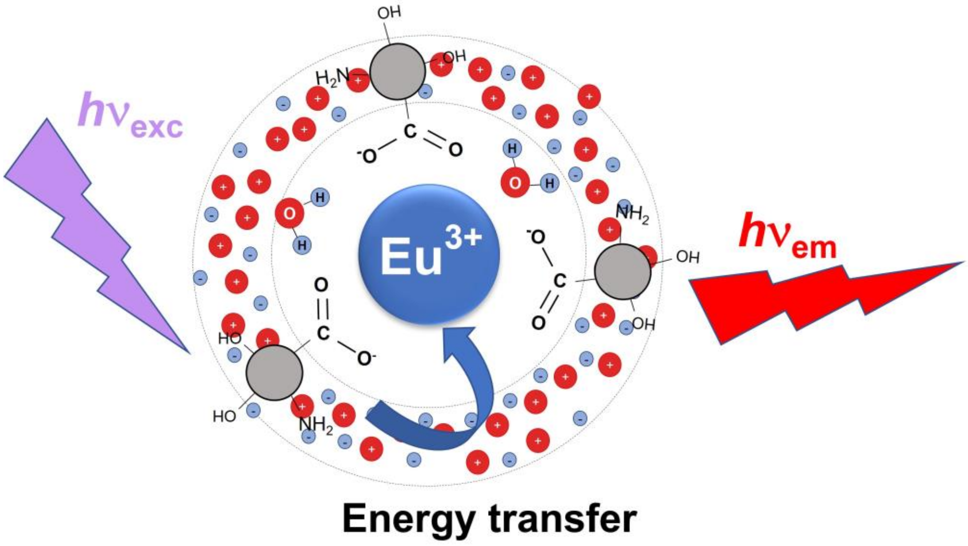
The intriguing photophysical properties and biocompatibility of carbon dots (CDs) have allowed them to become one of the most popular nanosystems for a multitude of applications. Generally, the interaction of external substrates such as metallic cations[1] with CDs surface leads to the change of CDs optical properties. Here we used CDs, prepared from natural precursor, as complexing and sensitizing agents for Eu(III) cations. In the CDs-Eu^{3+} adduct, CDs luminescence is almost quenched and the absorbed energy is funnelled by energy transfer processes in the Eu(III) coordinated ions sensitizing their characteristic red luminescence (antenna effect) [2, 3]. Lanthanide ions were complexed from $-COO^-$ moieties on the surface of CDs that are pH sensitive. The CDs-Eu(III) complex was tested as a red emitting acidic pH sensor, reading the luminescence quenching at 700 nm operated by carboxylate protonation and consequent Eu^{3+} displacement. Red emission and particular sensitivity make this complex addressable also for bio-applications.



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Oral-O14

DASAs in liposomes for drug delivery: a proof of concept

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Donor–Acceptor Stenhouse Adducts (DASAs) are a new family of photochromes that lately gains more and more attention into the scientific community. These compounds present a groundbreaking property: switching from an open-colored form to a closed-colorless form with low energy visible-light excitation, their polarity also change, from apolar to polar [1]. This uncommon property opens the way for multiple applications of these new photochromes, such as photo-switch for controlled drug delivery.

Although some properties of DASAs in organic solvents have already been described [2], their behavior in aqueous solution [3] and furthermore their use with liposomes still need to be explored. For this purpose, formulation of DASAs in POPC liposomes has been investigated and FRET phenomenon between a fluorescent probe and DASAs' linear isomer has been used to localize the photochromes inside the nanostructure. Our results highlight that B8-8 DASA has been directly incorporated inside the liposome's lipids bilayer, and that its photoactivation leads to its release into the external aqueous medium. We also investigate the influence of different structural variation. This proof of concept is opening interesting opportunities for applications of DASAs in photo-induced drug release field and therefore in the treatment's improvement of various diseases.

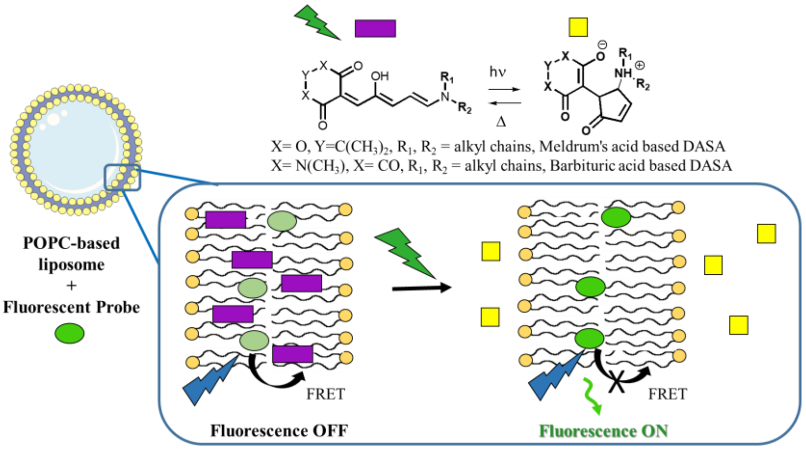

Fig. 1. DASA photo-isomerization in fluorescent-labelled liposome.

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Oral-O15

Investigation of Thermally Activated Delayed Fluorescence (TADF) Compounds in Photoredox Catalysis

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Organic photocatalysts present a solution to the issues of toxicity, abundance and cost associated with traditional transition metal photocatalysts. 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN),[1] a compound that exhibits thermally activated delayed fluorescence (TADF), has been employed widely as an organic photocatalyst owing to its appreciable visible light absorption, extended excited state lifetime and wide redox window.[2] TADF compounds typically contain donor and acceptor moieties that are weakly electronically coupled. As a result, the energies of the HOMO and LUMO can be modulated almost independently, giving rise to compounds with highly tunable redox potentials.

We report the investigation of photocatalytic systems[3] and the consecutive photoinduced electron transfer mechanism (ConPET)[4], where the photocatalyst is first reduced to radical anion, and then can be excited by a second photon to induce a much more powerful reducing species.

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Oral-O16

Looking for exciton interaction through peptide chains

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Covalently linked peptide-porphyrin compounds are very suitable systems for fundamental studies aiming at the comprehension of the mechanisms determining the efficiency of photoinduced energy/electron transfer (EnT/ElT) processes. Mimicking photosynthetic units, the porphyrin groups act as antenna moieties, while the peptide chain is the active medium through which EnT/ElT take place. In this contribution we studied the transfer of excitation between two identical tetraphenylporphyrin groups connected by short peptide chains of different length formed by non-coded conformationally constrained amino acids, *i.e.*, α-methylvaline (Figure 1). The photophysical events following porphyrin photoexcitation have been characterized from the microsecond to the picosecond time region by time-resolved spectroscopy techniques. Ultrafast transient absorption and anisotropy measurements revealed the presence of a new time component that we assign to exciton transfer through the peptide chains. Molecular Dynamics simulations suggest that the long lifetime of the exciton species is determined by the rigidity of the peptide chain, that inhibited energy relaxation pathways coupled to torsional motion around the dihedral angles of C^{α}-tetrasubstituted residues.

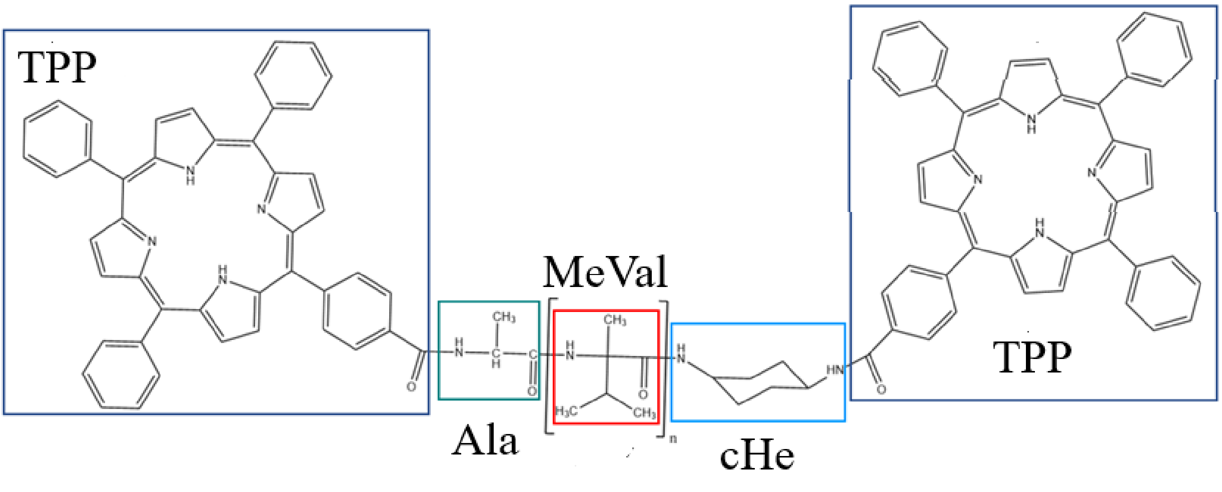

Fig. 1. Chemical structure of the bis-porphyrin-compounds investigated. n=2,4,6. The alanine (Ala) and cyclohexane (cHe) groups linking the porphyrin moieties to the α(methyl-)Valine $(MeVal)_n$, n=2,4,6 peptide chain are also shown.

These results open promising pathways toward the development of innovative materials for photodynamic therapy or bio-inspired Dye Sensitized Solar Cells.

Oral-O17

Charge Carrier Dynamics in $WO_3/BiVO_4$ Heterojunction Photoanodes

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Photoelectrochemical (PEC) water splitting converts solar light and water into oxygen and hydrogen, a clean energy vector. Bismuth vanadate, $BiVO_4$, is a promising ternary semiconductor oxide employed in photoanodes for the oxygen evolution reaction (OER) in water-splitting devices [1]. When coupled with WO_3, the $BiVO_4$ ability to absorb visible light up to 520 nm and the excellent electron transport properties of WO_3 allows the $WO_3/BiVO_4$ heterojunction photoanodes to perform much better than the separate oxide components [2].

In previous studies, we employed transient absorption spectroscopy (TAS) to investigate the charge carrier dynamics in the $WO_3/BiVO_4$ system. We observed the hole dynamics in $BiVO_4$ by monitoring transient changes in the visible range [3], and electron dynamics in the two oxides by monitoring the mid-infrared [4]. We also identified wavelength-dependent processes by tuning the excitation pump wavelength across the WO_3 absorption edge at ca. 450 nm [5]. These studies unveiled complex charge transfer processes. Indeed, the band alignment (type II) between the two oxides allows charge separation or recombination, depending on the excitation wavelength. Under visible light excitation of $BiVO_4$, electrons promoted in its conduction band (CB) flow into the lower-lying CB of WO_3, while holes remain in the $BiVO_4$ valence band (VB). This process (process A in Figure 1) decreases charge recombination and extends the lifetime of the charge carriers in the heterojunction, which is beneficial for PEC performance. Conversely, irradiation at wavelengths below 450 nm leads to the excitation of both oxides, opening a detrimental recombination path between the electrons photopromoted in the CB of WO_3 and the holes in $BiVO_4$ (process B in Figure 1).

We recently found that exploiting the $BiVO_4$ layer to sensitize WO_3 to visible light and shielding it from direct photoexcitation overcomes this efficiency loss [6]. These findings suggest methods to suppress undesired wavelength-dependent recombination processes and optimize charge transport in semiconductor devices based on heterojunctions.

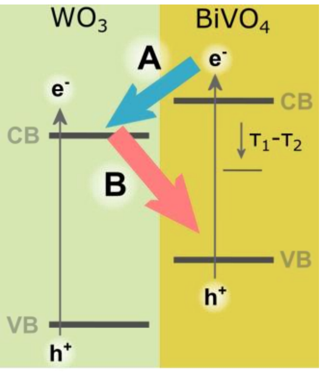

Fig. 1. Charge carrier transfer paths in the $WO_3/BiVO_4$ heterojunction: light absorption in $BiVO_4$ generates holes h^+ in the valence band (VB) and electrons e^- in the conduction band (CB). Electrons can recombine with holes (with time constants τ_1 and τ_2) or flow into WO_3, leading to charge separation through process A. When WO_3 is photoexcited, electrons in its CB can recombine with holes in $BiVO_4$ via process B.

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Oral-O18

Spotlight on the Photobehaviour of Push-Pull Compounds: hints of Singlet Fission

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Singlet fission (SF), the down-conversion of a singlet excited state in two independent triplet excitons, has recently aroused great interest as it promises to boost solar cells efficiency beyond the Shockley-Quisser limit [1, 2]. Despite the tremendous research effort, the number of SF-capable chromophores is still limited to a few classes of compounds, namely acenes, perylene/terrylenedimides, diphenylisobenzofurans, diketopyrrole-pyrroles. More recently, much of this effort has been directed to homo or hetero-dimers of the prototypical SF systems and donor−acceptor (DA)-type conjugated polymers. This is because the intramolecular SF is more attractive as allows for better control of its efficiency, being insensitive to the intermolecular packing, and facilitates the processing technics when dealing with photovoltaic applications.
In light of expanding the pool of SF materials, the photobehavior of several organic, conjugated push-pull compounds has been thoroughly investigated by mean of steady-state, fast and ultrafast spectroscopies. Particularly, the presence of the peculiar intermediate species, known as correlated triplet pair or double triplet or biexciton state [3], having triplet nature but overall singlet spin multiplicity, was probed by femtosecond transient absorption and emission spectroscopies. Among the other competitive deactivation pathways, the possible involvement of SF in the excited state dynamics was thus taken into consideration. To gain mechanistic insight, the impact of different solvent properties, concentration, molecular structure on the photobehavior of these compounds in solution and on the SF process was carefully addressed through less conventional spectroscopic techniques. This study attends to guide the design of new synthetic strategies for potential SF candidates.

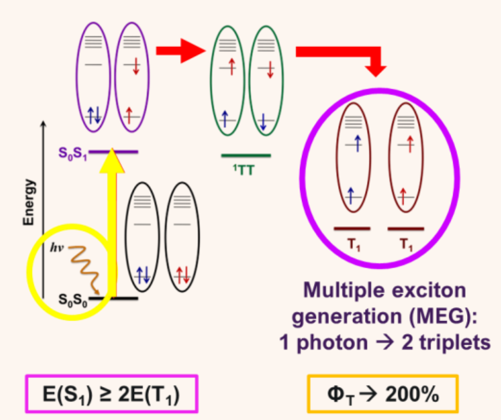

Fig. 1. Schematic overview of SF process.

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Oral-O19

Protein aggregation detection with a fluorogenic hyaluronan-based probe

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Proteins are natural polymers based on a library of 20 L-a-amino acids folding into defined structures to acquire biological active functions. Despite the native fold is the thermodynamically favoured conformation, variations in the pH, temperature, oxidative stress, crowding effects or interaction with other biomolecules can lead to new unstable conformations characterized by lower colloidal stability with a tendency to aggregation and/or phase separation.[1] Protein aggregation is a phenomenon strictly related to the incidence of severe human neurological disorders [2] and has also been observed in different model organisms including bacteria and plant cell cultures, correlated to stress conditions. In this context, the development of methods for a deep monitoring and comprehension of the molecular pathways of protein aggregation is vital for the early detection of pathological hallmarks and a full understanding of the cellular use of this phenomenon.

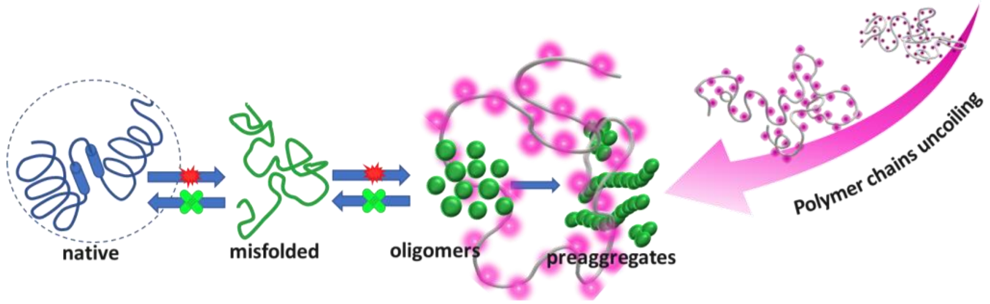
In our work we studied the interaction of a model plant derived metabolic enzyme GAPC1 undergoing oxidative-triggered aggregation with the fluorogenic biopolymer HA-RB, i.e., hyaluronan functionalized with Rhodamine B.

In aqueous solution, HA-RB forms nanogels, in which the dyes are confined in hydrophobic pockets, where both inter- and intra-filament fluorophores interact to cause massive fluorescence self-quenching.

Upon interaction with the protein aggregate, HA-RB nanogels change conformation, the self-quenching interactions are broken, and HA-RB becomes brightly emissive, allowing to follow the aggregation kinetic with spectrofluorimetric essay.

Interestingly, compared to traditional fluorescent probes such as ThT and to light scattering measurement, the HA-RB emission signal starts to rise much earlier, during the so-called lag-time. This early diagnostic ability of HA-RB evidences the potential of this probe to interact with early oligo/pre-aggregates of the protein, a significant feature both in diagnostics and therapy.

We discuss the origin of the ability of HA-RB as stemming from an interplay of the polymeric nature of the scaffold and of the fluorogenic mechanism of the probe.



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Oral-O20

Insights into the luminescence properties of persulfurated benzenes

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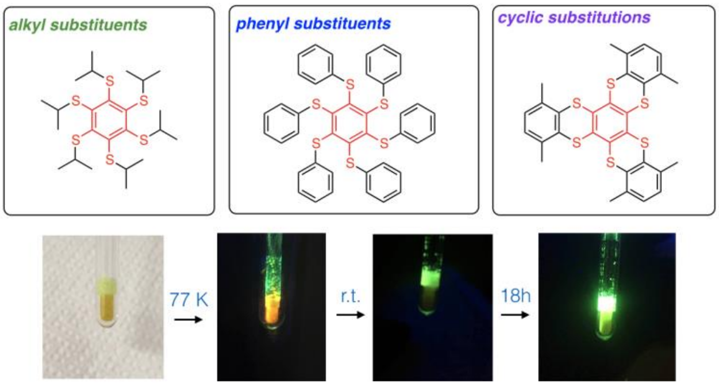
High intensity and long-lasting room temperature phosphorescence from molecular solids is regarded as one of the most intriguing properties for molecular materials, due to their countless application in information security, biological imaging, optoelectronic devices, and intelligent sensors [1]. Despite the relatively large amount of known and available organic phosphors, the design of emissive solids at room temperature and the full comprehension of the photophysical phenomena affecting the lumincescence performances of such emitters still represent a challenging task. Phenyl-substituted persulfurated benzenes have been reported as strong organic phosphorescent emitters in the solid state at room temperature [2-3]. Recently, we have taken into account a small family of phenyl-, alkyl-, and polycyclic substituted persulfurated benzene in order to rationalize their behaviour as organic emitters [4]. We investigated in detail the photophysical properties of these materials both in solution and as solids at room temperature and at 77 K, highlighting that for phenyl-substituted molecules an intense green emission is observed from solids at room temperature and in frozen solutions. Differently, the phosphorescence of alkyl-substituted compounds detected at low temperatures is dependent on the physical state of the sample. Moreover, the analysis of the luminescence of amorphous samples at low temperature has evidenced an intricate combination of several factors – *i*) presence of intermolecular interactions, *ii*) conformational disorder, and *iii*) nature of the electronic transition involved – that has been elucidated with the help of theoretical calculations.



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Oral-O21

New photosensitizers based on MSNs and PLGA nanoparticles incorporating cyanines and squaraines for Antimicrobial PDT

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The wide spread of antibiotic resistance is closely connected to the high index of human morbidity and mortality, as well as hospital costs. The developed antibiotic resistant strains of bacteria to conventional antibiotic therapy imply the demand for alternative treatments for infectious diseases. One strategy that may lead to improved antimicrobial treatment is the application of antimicrobial photodynamic therapy (aPDT). Among different PSs, polymethine dyes (PMDs), i.e. cyanines (CY) and squaraines (SQ), are retaining attention in a wide range of applications of science and technology, including PDT [1] and also in a very few examples of aPDT. The advantage of PMDs over other classes of PSs relies in the possibility of easily tuning their structure to obtain the proper photophysical and photochemical properties for the desired application. However, the highly efficient PMDs are generally hydrophobic causing self-aggregation of the PS under physiological conditions, detrimental in view of an efficient aPDT as it diminishes ROS generation capability. To overcome these drawbacks, a possible solution would be the incorporation of these dyes inside nanoparticles (NPs), which, in addition to preventing the formation of dye aggregates in aqueous media and protecting their photochemical characteristics, have shown an important role in the treatment of infection [2,3].

The present work deals with the design and development of innovative nanophotosensitizers based on Mesoporous Silica and PLGA Nanoparticles incorporating SQs and CYs with different structural features, with potential application in aPDT. NPs-dye complexes were characterized by DLS, NTA, FE-SEM, UV-Vis and fluorescence spectroscopy, exhibiting size ranging between 150 and 200 nm, excellent optical properties and remarkable photostability. In addition, their ability to produce Reactive Oxygen Species (ROS), which could produce bacterial death, was evaluated. The results proved that ROS generation ability is preserved in NPs-dye complexes. Furthermore, *in vitro* antimicrobial activity studies against Gram-negative and Gram-positive model bacteria in planktonic state were conducted to evaluate the potential of these nanophotosensitizers for aPDT in the local treatment of infections.

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Oral-O22

Photoelectrochemical decatungstate-catalyzed alcohols oxidation

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Photocatalyzed hydrogen atom transfer (HAT)[1] is a powerful tool in organic chemistry for the smooth manipulation of C–H bonds via highly reactive radical species. Our group is interested in the development of methodologies based on this reaction manifold through the use of tetrabutylammonium decatungstate (TBADT, $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{W}_{10}\mathrm{O}_{32}]$)[2] as the photocatalyst (**PC** in Fig. 1). Upon irradiation, the excited **PC*** cleaves homolytically the C–H bonds in a variety of organic derivatives (R–H),[2] being converted in a singly-reduced form featuring one extra electron (**H-PC$^\bullet$**, $\mathrm{H}^+[\mathrm{W}_{10}\mathrm{O}_{32}]^{5-}$). Intriguingly, the merging of photocatalysis and electrochemistry offers a smart option to turn-over the spent **PC**, avoiding the need to employ a (sacrificial) chemical oxidant.[3,4]

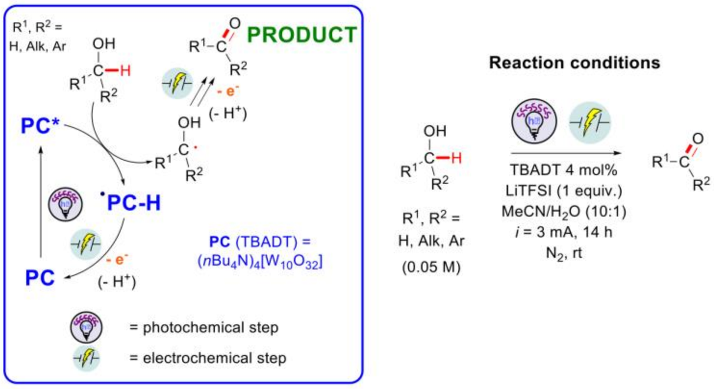

Fig. 1. Mechanism of decatungstate-catalyzed photoelectrochemical oxidation of alcohols.

Along this line, we hereby report our recent results in the realization of net-oxidative, photoelectrochemical processes based on decatungstate photocatalysis. Thanks to this strategy, we developed a strategy for the mild oxidation of both benzylic and aliphatic alcohols (either primary or secondary) under chemical oxidant-free conditions, selectively leading to the corresponding carbonyls.[5]

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Oral - O23

Mechanistic Insights Into Nickel-Mediated Enantioselective Photoredox Allylation Of Aldehydes

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Photoredox catalysis aims at obtaining challenging products by means of a series of photoinduced electron transfer events that are triggered by the combination of a photosensitizer with a suitable catalyst [1].

Thanks to this approach, we developed a procedure to carry out the allylation of aldehydes promoted by a fully organic photosensitizer, an earth-abundant nickel catalyst and visible light. In addition, the presence of a chiral ligand on the nickel catalyst allows us to control the enantioselectivity of the reaction [2].

Photophysical studies include the characterization of the photosensitizer and clarification of the nature of the nickel catalyst and, finally, quenching experiments enabled the determination of the mechanism of the reaction.

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Oral-O24

Design of Experiments in organic synthesis: optimization of a doubly photochemically activated bicomponent reaction

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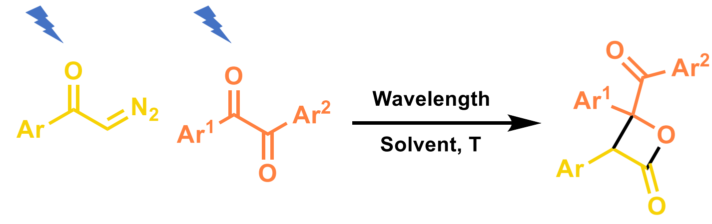
The use of chemometrics is an attractive strategy to find the real optimum in chemical reactions. Design of Experiments is a multivariate method that allows to study and define the interactions between the variables of the system performing a reasonable number of experiments, differently from the *One Variable at Time* (OVAT) method [1]. It is extensively used in industry, but recently it has gained increasing interest in organic synthesis. Furthermore, through a chemometric approach, it is possible to extract high quality information from less resolved data [2].
The novel methodology reported in this contribution was developed for the synthesis of β-lactones. It involves a Paternò-Büchi Reaction between a ketene and a 1,2-diketone, promoted by a double photochemical activation under visible-light (Fig. 1a) [3]. An investigation of the optimal reaction conditions was performed using a design of experiments (DoE). This study started from defining the four-process variables playing an important role in the reaction, in particular wavelength, solvent, temperature, and number of equivalents of diketone (Fig. 1b). Many *ad hoc* designs were realized to identify the interaction between the process parameters and the optimal reaction conditions. Moreover, the versatility of the reaction was tested.
This is an uncommon approach employed in organic synthesis, even though it entails various advantages under different points of view [4].

a)



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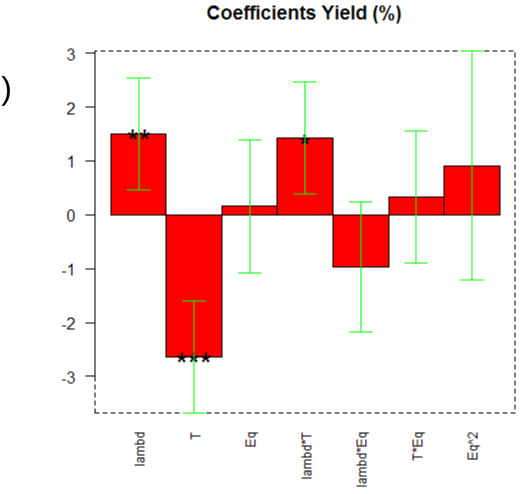

Fig. 1. a) General doubly photochemically activated Paternò-Büchi Reaction; b) Example of Coefficients Yield plot of the studied system.

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Oral-O25

Translation of photooxygenation reaction of aromaticmolecules from organic to aqueous environment: challenges towards a preparative protocol

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With the aim of developing green synthetic protocols for the photooxygenation of hydrophobic molecules in water, a combination of supramolecular and photo-chemistries was exploited. The photochemical synthesis of aromatic endoperoxides is a very well-known and established procedure for the storage of molecular oxygen to be exploited *in situ* in biological applications. In fact, the mechanism bringing to the formation of this bridge is reversible and tunable, enabling the release of molecular oxygen or reactive oxygen species (ROS) according to the molecular structure. We optimized the photochemical synthesis of selected aromatic endoperoxides in organic solvents in the presence of a photosensitizer, *i.e.* Methylene Blue (MB), catalyzing the covalent link of singlet oxygen (^{1}O2) onto the aromatic backbone. The same reaction was then translated to aqueous environment after inclusion complexation of the substrates and MB in a cyclodextrin-based polymeric network. The same performance was achieved in the same reaction conditions, allowing the application of a greener procedure for upscaling. The release of ^{1}O2 and ROS was achieved by thermolysis of the formed endoperoxide bridges irrespectively of the environment in which they were obtained and subsequently heated. These preliminary results pave the way for future development of photodynamic therapy (PDT) in hypoxic conditions, *i.e.* when inside solid cancer cells it is not achieved an adequate supply of O2, reducing the standard PDT efficacy.

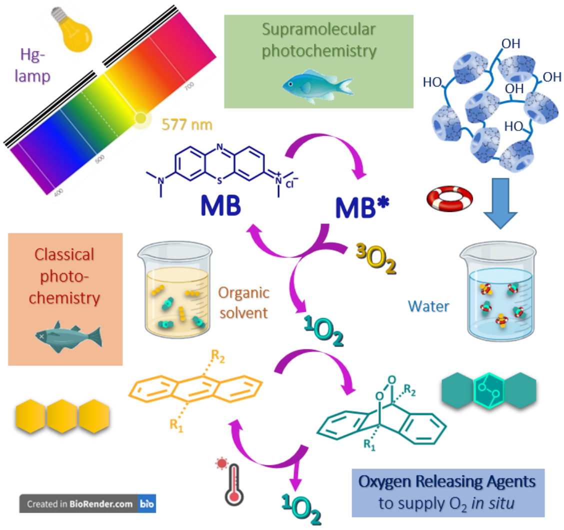

Fig. 1. Scheme for the photooxygenation of aromatic hydrophobic substrates in organic solventand water after supramolecular interaction with cyclodextrin-based polymers.

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Flash-F1

Selective light-driven CO_2 reduction with a hexadentate polypyridine Iron(II) catalyst

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Fossil resources are receding while the global energy demand increases. The development of noble-metal-free catalysts capable of converting carbon dioxide selectively into value-added compounds remains one of the central challenges in catalysis research [1]. Biological and heterogeneous catalysts for the electrochemical CO_2 reduction (CO_2RR) reaction often exhibit a high degree of electronic delocalization, useful in minimizing overpotential and maximizing selectivity with respect to competitive pathways of the hydrogen evolution reaction (HER) [2].

Here, we report a molecular catalyst based on an iron(II) complex that follows this design concept in a homogeneous setting through the use of the redox non-innocent DBPy-PyA (1-([2,2'-bipyridin]-6-yl)-*N*-([2,2'-bipyridin]-6-ylmethyl)-*N*-(pyridin-2-ylmethyl)-methanamine) ligand [3]. In particular, the electrochemical characterization in ACN/H_2O mixtures showed low overpotentials toward CO_2RR and excellent selectivity towards the formation of CO. Application under photochermical conditions with $Ru(bpy)_3^{2+}$ as the dye and N,N-diisopropylethylamine (DPEA) as the electron donor confirms over 90% selectivity and good stability.

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Flash-F2

A commercial catalyst for media-independent H_2 evolution

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Energy harvested directly from sunlight can fulfill the need for clean energy, and its conversion into hydrogen represent the most promising alternative to fossil fuels. Since then, a robust, efficient and cost-effective *Hydrogen Evolution Catalyst* (HEC) is of paramount importance to push the hydrogen-based energy technologies [1]. In view of that we investigated the behavior of commercially available ruthenium oxide (RuO_2), usually employed as *Oxigen Evolution Catalyst* (OER) [2,3] and mostly in electrocatalysis, with the well-known photochemical system based on ruthenium tris-bipyridyl ($[Ru(bpy)_3]^{2+}$ photocatalyst) and methyl viologen (MV^{2+} electron relay) [4]. In aqueous medium this catalyst gives exceptional hydrogen production rates using different sacrificial electron donors, including sulfur compounds that poison platinum, the HEC *par excellence* [5,6]. The most attractive feature of RuO_2 lies in its versatility, since it shows a very high activity also in organic media reaching, in case of acetonitrile, production rate very similar to the aqueous medium. This characteristic opens new possibilities for hydrogen production, allowing to use useful oxidation reactions, like organic pollutants as electron and hydrogen sources instead of sacrificial donors.
Furthermore, ruthenium oxide is completely recoverable by simple centrifugation and its activity remains unchanged after various cycles in different media.

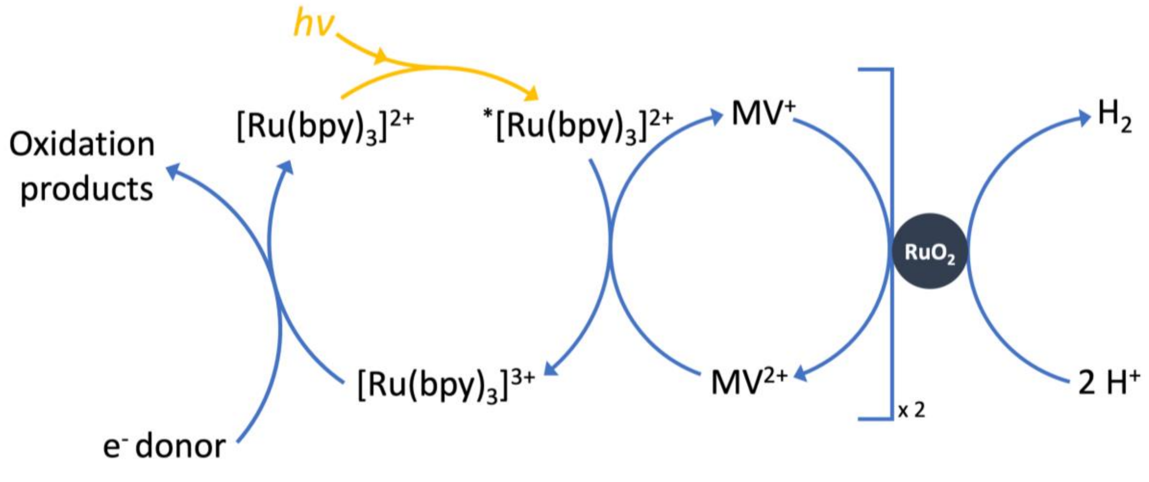

Fig. 1. Scheme of the photocatalytic cycle employed to test RuO_2 performances.

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Flash-F3

Molybdenum doped $BiVO_4$ as visible light sensitizer for TiO_2 photoanodes in solar water splitting

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Capturing and storing solar energy into hydrogen as clean fuel is a promising route to replace fossil fuels towards the development of a sustainable society. Photoelectrochemical (PEC) water splitting occurring at the semiconductor/electrolyte interface of both a photoanode and a photocathode in a tandem cell has emerged as effective strategy to this aim [1]. Identifying semiconducting materials acting as photoanodes for oxygen evolution with high efficiency and long-term stability is the major performance bottleneck of this device. TiO_2 is by far the most studied semiconducting metal oxide thanks to its remarkable stability and suitable band edge location towards both the anodic and cathodic semireactions. However, its relatively wide band gap of 3.2 eV strongly limits the exploitation of a large part of the solar light spectrum [2]. Coupling TiO_2 with a narrow band gap metal oxide, such as $BiVO_4$, would address this issue allowing for TiO_2 sensitization to visible light [3]. In this work, we propose a successful strategy to overcome the limits imposed by the unfavorable type I band alignment predicted at the interface of the two semiconductors in the $TiO_2/BiVO_4$ heterojunction, hampering the efficient separation of photogenerated electron-hole couples. A hot electrons injection mechanism from $BiVO_4$ to TiO_2 under visible light excitation, active only at $\lambda \leq 490$ nm, i.e., for incident photons with an excess energy with respect to the $BiVO_4$ band gap, was indeed found at the basis of its unexpected functionality [3]. The coupled system outperformed only with respect to the UV-absorber oxide, not to the pure $BiVO_4$ system (Figure 1). Differently, coupling TiO_2 with optimized molybdenum doped $BiVO_4$ determined a dramatic photoactivity increase of the resultant TiO_2/Mo:$BiVO_4$ heterojunction system with respect to both the undoped $TiO_2/BiVO_4$ composite material and each of the two single components (Figure 1). This impressive result can be explained by considering the establishment in the novel system of a staggered (type II) band edge alignment at the oxides interface. In particular, structural distortions of the $BiVO_4$ crystal structure [4] upon Mo^{6+} incorporation in the material bulk would play a key role for obtaining such band edges alignment, which may promote a beneficial visible light-induced charge carriers separation within the here investigated home-made heterojunction photoanodes.

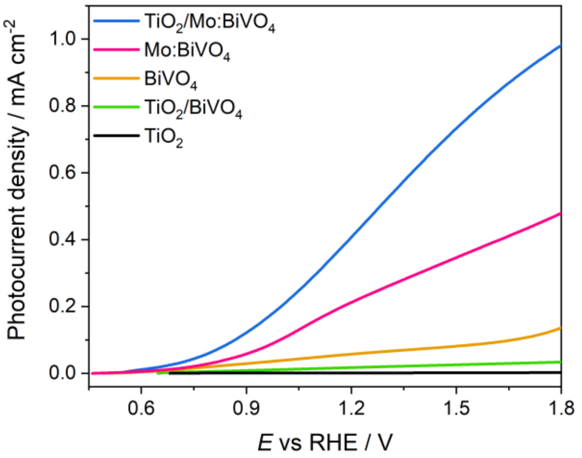

Fig. 1. LSV plots in 0.5 M Na_2SO_4 electrolyte under irradiation with $\lambda \geq 400$ nm through the electrode/electrolyte interface.

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Flash-F4

Composite CdS/TiO_2 powders as visible light responsive photocatalysts: relation between textural properties and photocatalytic activity

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Much scientific literature concerns the use of TiO_2 for various applications, as photocatalyst for pollutant degradation, for DSSC, for gas sensors, batteries, etc. In fact, it has good stability, low cost, and low toxicity; however, the main disadvantage is the wide band gap that allows only 5-6 % of the solar spectrum to be exploited [1]. On the other hand, CdS has a smaller band gap, but it is characterized by a very low photostability. The combination of CdS with TiO_2 to generate a composite material is of interest since the disadvantages of the two components can be overcome [2] [3]. In particular, the spectral response of CdS/TiO_2 system is extended to the visible region, and the position of the band edges allows the separation of charges upon illumination of CdS with visible light and subsequent injection of electrons from CdS to TiO_2. This increases lifetime of separated charges and could also have a positive effect in photocatalysis.

In this work, we report about the synthesis of a series of composite CdS/TiO_2 powders that were successfully prepared by hydrolysis of a titanium alkoxide on colloidal CdS [4]. Textural characterization (XRD, HRTEM, FESEM, EDS) evidenced the presence of anatase crystalline domains (of nanometric size), and of homogeneously dispersed CdS particles (acting as seeds for anatase growing). The intimate contact between CdS and TiO_2 is confirmed by the analysis of the emission decay time with the longer lifetimes of separated charges in the larger crystalline materials.

A correlation among textural characteristics and photocatalytic properties pointed out that nanometric size of anatase crystalline domains, presence of dispersed CdS, and presence of mesopores as nanoreactors, where the intimate interaction surface/reactant occurs, are necessary for obtaining a noticeable photoreactivity in the reductive transformation of 4-nitrobenzaldehyde to the corresponding aniline.

In addition, the combination of TiO_2 with CdS increases the photostability of the photoactive material, thus opening the possibility of photocatalytic transformations under visible light conditions.

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Flash-F5

Polyquinoid Dye-Cobalt Oxide Hybrids: Novel Rare Metal-Free Dyads for Photoelectrochemical Water Oxidation

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Artificial photosynthesis is a promising strategy for conversion of solar energy into chemical feedstocks. In this context, dye-sensitized photoelectrochemical cells (DS-PECs) have achieved a key role as devices to drive solar light-promoted water splitting. Herein, we present novel, completely rare metal-free hybrid dyads composed by organic dyes and Co_3O_4 nanoparticles as water oxidation catalyst (WOC) on *meso*-SnO_2 photoanodes. The dyes belong to the unique class of KuQuinones (KuQ),[1–3] displaying wide absorption in the visible range, and characterized by a highly oxidizing excited state while managing proton-coupled electron transfer events. KuQ was bound through a phosphonate anchor to $Co_3O_4^{heptOH}$, 3 nm particles stabilized by a heptanol shell synthesized *via* a finely controllable organometallic approach.[4] The hybrid KuQ/Co_3O_4 dyads were studied under visible light irradiation, upon deposition on *meso*-SnO_2 films (Figure 1) and proven competent in promoting photoelectrochemical oxygen evolution, with Faradaic efficiency for O_2 evolution close to 90% and 0.44% IPCE at 510 nm.

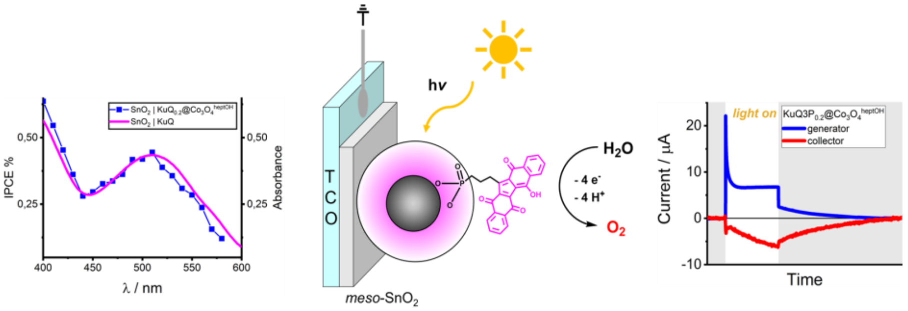

Fig. 1. Schematic representation of the O_2-evolving photoanode based on the hybrid particles on a transparent conductive oxide (TCO)/*meso*-SnO_2 electrode.

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Flash-F6

Living photosynthetic bacteria for sustainable bio-photovoltaics

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Solar energy is the most abundant energy source for planet Earth and the development of solar power technologies is considered one of the best options to meet the increasing future energy demand [1].

Photosynthetic organisms such as plants, algae and some bacteria are the sole biological entity able to exploit sunlight to synthetize energy-rich compounds from abundant but thermodynamically stable inputs like water and CO_2. They have been finely tuned over billions of years of evolution to manage photon capture and conversion processes. The study of the photosynthesis and of its mechanisms provide important insight about fundamental mechanisms of photochemical energy conversion that, in turn, has inspired researchers to develop semi-artificial photosynthetic systems based on whole living organisms and non-biological interfaces [2].

Rhodobacter (R.) sphaeroides is a versatile photosynthetic purple non sulphur bacteria able to harvest sunlight, and particularly the Near Infrared region, and perform an efficient photochemical energy transduction [3]. The charge-separated state generated in the photoenzyme known as reaction center (RC) is the driving force for the metabolism of the bacterium. Previous attempts to integrate the sole RC in electronic devices successfully resulted in photovoltage generation and in direct photomodulation of the output current of electrolyte-gated organic transistors [4, 5].

Here we present the exploitation of whole metabolically active photosynthetic microorganisms to photo modulate the current of hybrid bio-optoelectronic organic devices, overcoming the limiting multistep enzyme extraction, isolation, and purification and paving the way towards novel symbiotic strategies for environmentally safe and cost-effective energy production.

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Flash-F7

Development and synthesis of Bi based nanomaterials supported on graphene for photocatalysis

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The excessive use of fossil fuels has led to great global energy crisis and environmental problems. Solar energy, as a clean, sustainable and abundant energy source, has increasingly attracted attentions [1]. Since the landmark event that Fujishima and Honda discovered the UV-assisted catalytic water splitting on a TiO_2 electrode in 1972, photocatalysis has become a promising process to convert solar energy into chemical energies, so as to possibly overcome the energy shortage crisis.

Owing to its large bandgap (3.12 eV), TiO_2 is only active in the UV region and easily undergoes electron-hole pair recombination [2]. Recently, visible-active photocatalysts, such as bismuth-based catalysts like Bi_2WO_6, BiOBr, Bi_2O_3, Bi_2MoO_6 and so on have been attracting attention due to their utilization of solar light for photocatalysis.

In particular, Bi_2O_3, a p-type metal oxide semiconductor with a narrow energy gap of 2.85-2.58 eV has gained considerable attention due to its high refractive index, dielectric permittivity, thermal stability, and nontoxicity as well as wide application range [3-5].

However, using pure Bi_2O_3 as a photocatalyst has some drawbacks, such as relatively low photocatalytic activity and a high electron-hole pair recombination rate. To overcome this problem, it is necessary to modify the surface, identify defects, creating heterojunction or doping Bi_2O_3 to obtain a more effective and efficient photocatalyst.

Recently, graphene, a single-atom-thick sheet composed of *sp*2-hybridized carbon, has attracted tremendous interest in physics, materials science, and chemistry because it has several unique properties such as high surface area, excellent electrical conductivity and good light transmission [7]. In addition, graphene can act as an efficient electron mediator for heterojunction photocatalysts by extending the interface to the whole surface area of graphene sheets, which extremely facilitates the charge migration in the heterojunction structure, thus prolonging the lifetime of photogenerated charges [8].

In this study, we report the loading of different phase of Bi_2O_3 on graphene sheet through the dispersion in polybutadiene and the consequent formation of heterojunctions resistant to humidity. The resultant materials were characterized using various techniques and examined as photocatalysts for the fixation of N_2.

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Flash-F9

Photoelectrochemical properties of $WO_3/BiVO_4/Ag_2O$

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n-n junctions based on $WO_3/BiVO_4$ are among the most promising materials for photoelectrochemical cells (PEC) aimed at the conversion of solar energy into chemical energy. Typically this is achieved through the water splitting reaction resulting in the formation of oxygen and hydrogen at the photoanode and cathode side of the PEC respectively. However, OER is a multielectronic reaction which requires high overvoltage and the modification of the $WO_3/BiVO_4$ with overlayers favouring the OER may be decisive in a further improvement the PEC performance(a), particularly by reducing the need for externally applied electrochemical bias.Herein we report about the photoelectrochemical properties of $WO_3/BiVO_4$ photoanodes modified with silver oxides which could be readily obtained upon deposition of silver on top of $WO_3/BiVO_4$ via a 2step electrodeposition procedure. Morphological and XPS investigations point to the presence of a discontinuous Ag(I) layer which is converted, in part, to Ag(II) upon operation of the photoanode under polarization. Current/Potential (J/V) measurements shows a 200 mV negative shift (Fig.1) of the photoanodic onset potential and a general increase in the photocurrent produced by the junction. Differently than the unmodified $WO_3/BiVO_4$, hydrogen peroxide was the major product of the water splitting reaction, making $WO_3/BiVO_4/Ag_xO$ (x= 1 or 2) interfaces potentially suitable for the oxidative degradation of organic contaminants(b) combined to hydrogen evolution.

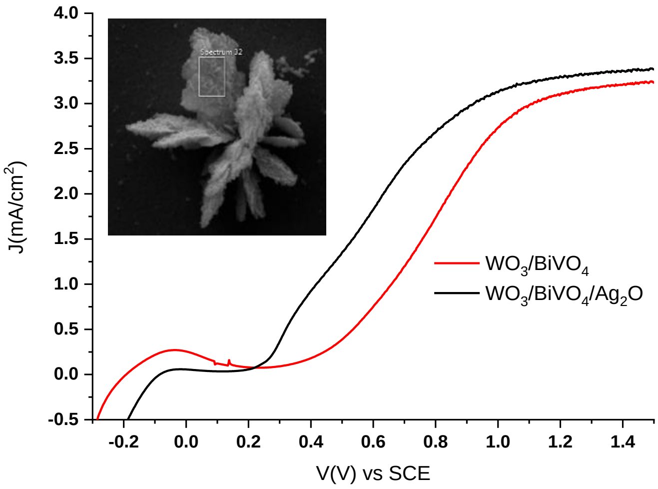

Fig.1 J/V curves under simulated solar light illumination

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Flash-F9

1qaA Cyclodextrins Based Fluorescent Supramolecular Nanoassembly for Combined Photo-Chemotherapy

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

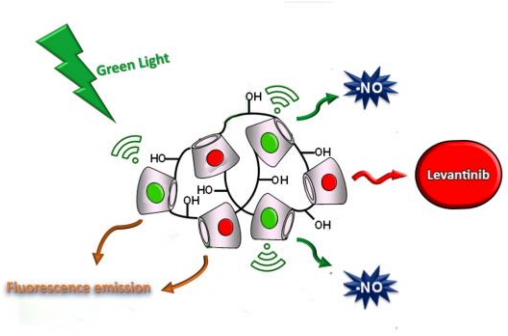

Fig. 1. *Schematic representation of the supramolecular construct.*

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Flash-F10

Fluorescent chitosan probes towards the detection of microplastics in complex environmental samples

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Plastics environmental pollution is exponentially increasing. Larger plastics, micron-sized fragments and nanoplastics (MNPs) constitute a serious concern from the ecological point of view [1][2]. Despite above all smaller-sized plastics raise considerable toxicological concern also for humans, regulatory and analytical methodologies for their complete identification and quantification are still missing [3].

We have recently developed a protocol to functionalize a biopolymer, hyaluronic acid, to obtain a fluorogenic probe for the detection of MNPs [4]. The so-obtained rhodamine B doped hyaluronan nanogels work as an off-on probe, that are self-quenched in solution, and recover their fluorescence upon interacting with the surface of MNPs (**Fig. 1**).

To overcome possible stability constraints related to hyaluronic acid we decided to explore the derivatization of another biopolymer, chitosan, with different fluorescent moieties to tune not only the emissive properties of the system but also its affinity toward the various microplastics.

We are building up a library of such multichromophoric biopolymers that can best deal with the analysis of complex environmental samples, aiming to move towards a co-staining approach with multiple probes: in this way it is possible to overcome the problem of non-selective interaction of the probes with different interferents and to exploit a composed color signal to discriminate plastic pollutants from various organic and inorganic interferents.

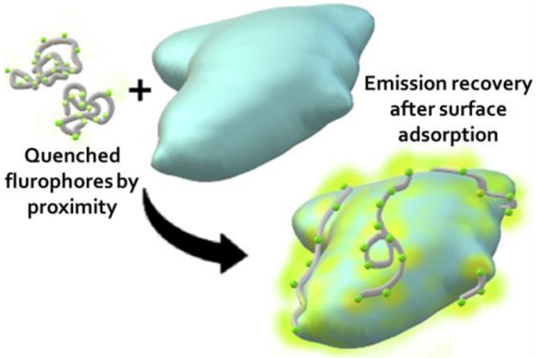

Fig 1. Working principle of polymer-based off-on fluorescent probe

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Flash-F11

Photoactive liposomial structure based on BODIPY and Curcumin subunits

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In this work, we present a novel photoactive liposomial system, that consists of BODIPY (difluoroBOron-DIPYrromethenes) and Curcumin subunits. In the steadily expanding field of fluorescent dyes, BODIPY have received attention because of their excellent stability, good solubility, intense absorption profile and high fluorescence yield; [1][2] in addition, their photo-physical properties can be easily tuned by modification of their backbone. Curcumin is a yellow pigment, with a highly delocalized π-electron symmetric structure, that possesses good optical properties, [2] and the results of some studies show that it has several pharmacological activities, such as antimicrobial, anticancer and antioxidant properties. On the other hand, Curcumin is photo-chemically unstable and pH-sensible.

Here, we report the preparation of a liposomial structure based on a suitably functionalized BODIPY and Curcumin (**Fig. 1.**). Both the supramolecular system and individual subunits were characterized and in particular, the photophysical studies demonstrate that in the multicomponent system takes place a photoinduced intercomponent energy-transfer process, from Curcumin to BODIPY. Moreover, Curcumin play the role of ROS scavenger in the supramolecular multicomponent assembly, if irradiated in the red.

This architecture could mimic ROS scavengers and the stress signaling of the antenna system in the photosynthetic machinery, in order to avoid antenna overload and subsequent damage.

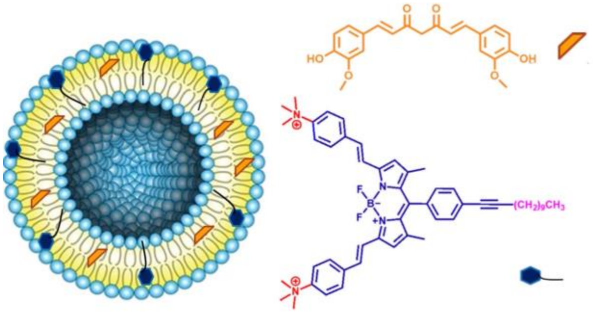

Fig. 1. Liposomial structure based on BODIPY and Curcumin subunits.

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Flash-F12

Autonomous Non-Equilibrium Operation of a Mechanically Interlocked Molecular Shuttle

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Nanoscale devices activated by light as a clean and highly controllable energy source can enable ground-breaking applications in technology and medicine.[1] Artificial molecular machines that exploit light energy autonomously to generate continuous motion are particularly appealing, especially for energy conversion purposes.[2] However, advances in the construction of such molecular architectures are highly challenging and only a limited number of systems have been reported to date.[3]

In light of this, we developed a [2] rotaxane composed of a crown ether macrocycle threaded by an axle embedding pH-sensitive and photoactive recognitions sites. In this system, the mechanical interlocking of the molecular components enables reversible and continuous ring shuttling between the extremities of the axle as a result of the entanglement of photoinduced isomerization and proton transfer processes.[4]

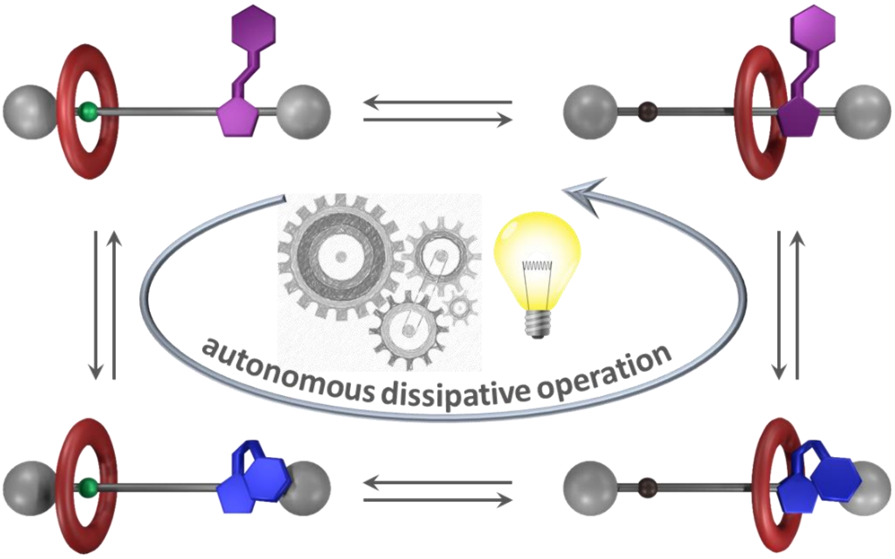

Fig 1. Closed network of reactions connecting the four states of the [2]rotaxane system.

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Flash-F13

Photo-catalyzed generation of glycosyl radicals for selective addition to electron poor double bonds; an access to C-glycosyl amino acids for glycopeptides synthesis

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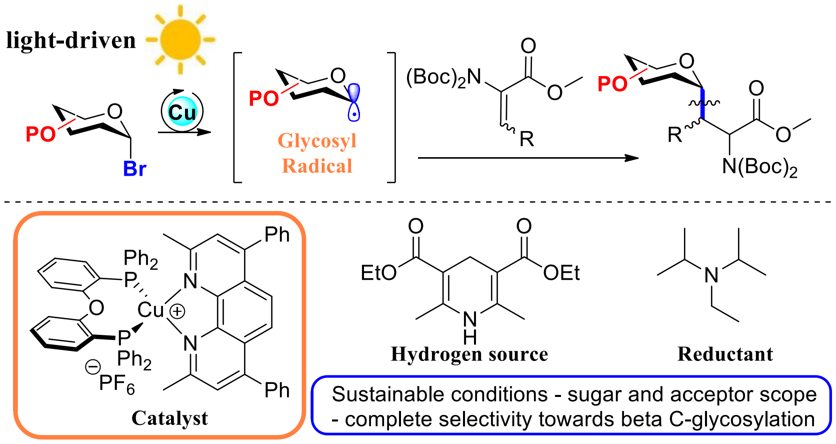
Herein we present the selective addition of glycosyl radical to dehydroalanine analogues to afford high valuable C-glycosyl amino acids promoted by photocatalysis. C-Glycosyl peptides are well-known mimics of the native glycoproteins; they differ from these last ones for stable C-C linkages instead of O/N-C bonds, that make them more metabolically stable and suitable for therapeutical purposes [1]. C-Glycosyl amino acids can be employed in this regard to install sugar fraction on the target peptides and proteins; thus, operational simple protocol to access these compounds is always welcomed. Inspired by literature on stoichiometric and catalytic generation of glycosyl radical to form C-C bond with electron-poor olefins [2,3], we envisaged the possibility to exploit photo-catalysis to generate the glycosyl radical which could be sequestered by electron-poor bis-BOC protected dehydroalanine derivates affording the resulting protected C-Glycosyl amino acids. We optimized the reaction conditions with the screening of different photocatalysts, solvents and reductants/additive. Cheap and easily to prepare Copper complex, shown in Scheme 1, has been found to afford the desired products in up to 100 % of yield (15 examples) in Water/MeCN mixture. The scope extension has been investigated varying the sugars, protecting groups and the electrophile. Furthermore, photophysical measurements have been performed to investigate the redox quenching and the mechanism.



Sustainable conditions - sugar and acceptor scope
- complete selectivity towards beta C-glycosylation

Fig. 1. addition of glycosyl radical to dehydroalanine analogues promoted by copper photocatalyst.

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Flash-F14

Supramolecular and Covalent Buildups of Melanin-like materials

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Melanin-like materials have found applications in fields of high social and economic impact as medicine and environmental remediation, since they can mimic the unique optical and electronic properties of the natural pigments, possessing also excellent biocompatibility.[1] Up to now, fundamental information about both natural and synthetic melanin, as the complete structure and composition of subunits, are still missing presenting a challenge for the scientific community.[2] Even if Polydopamine (PDA) is the most exploited melanin-mimicking material, a big debate about its structure hasn’t come to an end, as some have modeled PDA as supramolecular aggregates of monomers bounded through non-covalent interactions, while others suggested a covalent polymeric structure. Knowing that the oxidative-polymerization of dopamine (DA) in alkaline and aerobic conditions leads to the formation of a fraction of spherical PDA nanoparticles (NP), the genesis of populations other than NP was investigated. Indeed, exploiting Field Flow Fractionation (FFF) it was proved, for the first time, that PDA can emerge simultaneously in two different morphologies, a solid sphere (NP) and an entangled polymer. The two different PDA populations exhibited the typical broad-band absorption in the UV-Vis region of melanin materials, and it was proven that the polymer is formed upon oxidation of the NP as a result of a “size-focusing” process. Moreover, an extensive investigation in the first stages of PDA formation not only verified the presence of non-covalent self-assembly in PDA, but further proved the presence and the reversibility of a Charge-Transfer (C-T) adduct formed between unreacted DA and its oxidation product, indole-5,6-quinone(Q)(Figure 1).[3]

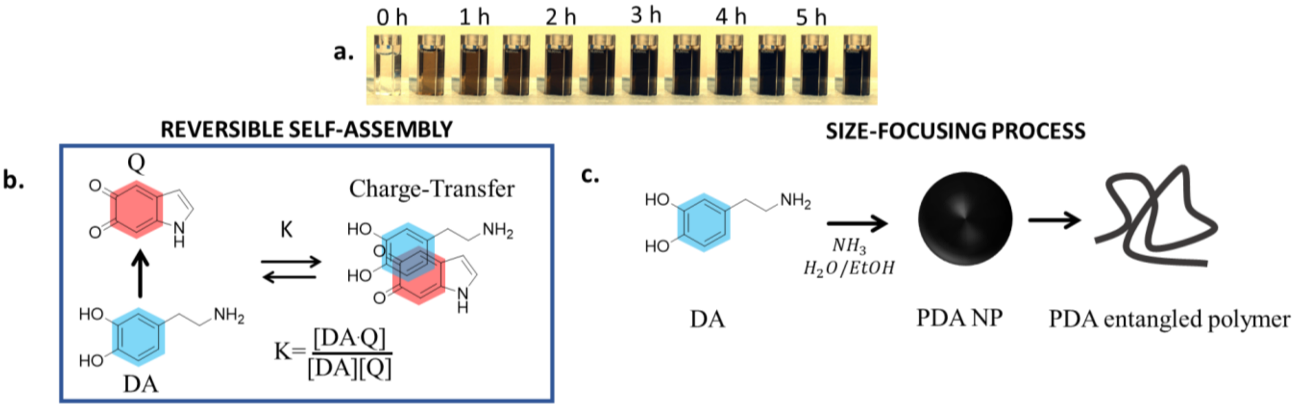

Fig.1. a) Dopamine (DA) polymerization and color change responsible for the characteristic broad absorption band; b) Reversible formation of C-T adduct involved in the first stages of PDA formation; c) Simultaneous presence of nanoparticles (NP) and polymer in PDA.

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Flash-F15

A photoactivated pseudorotaxane-based linear molecular motor

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Natural molecular machines exploit a source of energy to perform highly complex tasks,[1] analogously, artificial machines are able to perform work through the consumption of a fuel in a closed network of reactions.[2] Here we present the synthesis, and characterization of a linear molecular motor designed to achieve the directional transport of a crown ether macrocycle along a linear molecular component using light as the sole energy source. This machine is composed by two photoactivated "pump-modules" derived from a supramolecular pump motif recently developed in our group.[3] At the base of its operation is the $E \leftrightarrows Z$ photoisomerization of an azobenzene unit which causes the directional threading and de-threading of a crown ether rings along a molecular axle. In the dark, the linear motor self-assembles with macrocycles resulting in the formation of a pseudorotaxane, the subsequent irradiation of the system induces a release of the ring into the solution. The peculiar behavior observed is realized through an interconnected scheme of photochemical and complexation reactions whose consequence is to transduce energy of light into the directional movement of the ring.

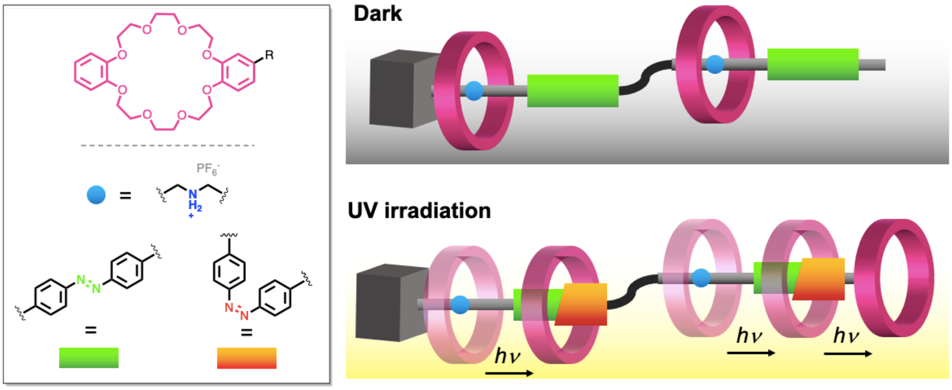

Fig 1. Left, molecular structures of the macrocycle and axle functional moieties. Right, graphical representation of the pseudorotaxane self-assembled in the dark and the ring release upon irradiation.

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Flash-F16

Towards an autonomous photochemically driven rotary motor based on a catenane

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By combining photophysical and photochemical reactivity with appropriately designed molecular and supramolecular systems, it is possible to realize nanoscale devices and machines that can execute sophisticated tasks in response to light stimulation.

In this regard, our group developed pseudorotaxane-based supramolecular pumps able to promote the relative unidirectional transit of non-symmetric molecular axles through macrocycles using only light as external stimulus [1]. More recently, the efficiency of such systems was highly improved through the fine tuning of the interactions between the axle and the ring components [2,3]. Research efforts are now oriented to the translation of the reactivity obtained for this minimalistic supramolecular architecture to more complicated mechanically interlocked molecules.

Here, we report the characterization of a [2] catenane designed to operate as an autonomous photochemically driven motor guided by isomerization and proton-transfer processes.

Our results suggest that, with this minimalist molecular design, it could be possible not only to control the relative unidirectional rotation of the rings, with a simultaneous light-induced thermodynamic and kinetic regulation on the system (energy ratcheting), but also to obtain an autonomous rotary motor, exploiting the photobasic behaviour of the molecule.

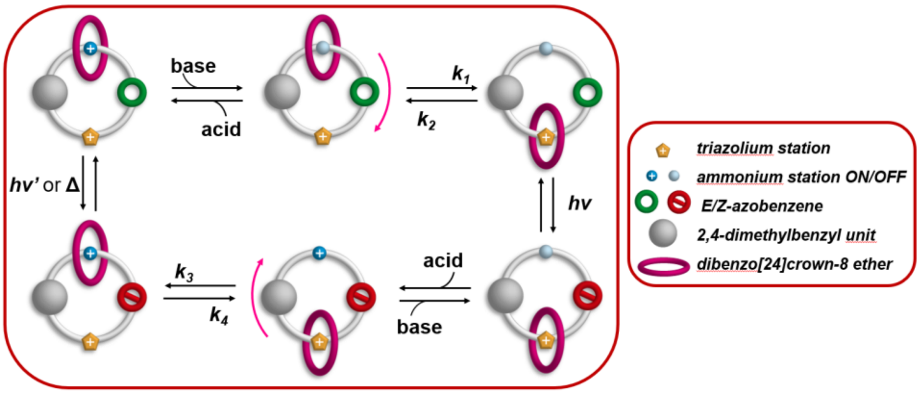

Fig. 1. Cartoon representation of the hypothetical operation cycle operated by the designed [2] catenane.

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Flash-F17

Photophysical properties of multi-responsive Bis(acridinium/acridane-porphyrin) Molecular Switches

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Most modern devices rely on multi-switchable systems for modular responses, which bring to different outputs. In this domain, a switchable bis(acridinium/acridane-porphyrin) conjugate, was designed to respond to different stimuli, namely electrons, nucleophiles and photons. The acridinium/acridane equilibrium is pH-dependent and significantly alters the photo- and electro-chemical properties.[1, 2]

The coupling of N-substituted acridinium units to Zn-porphyrins brings to fluorescence quenching of both moieties by an ultrafast electron transfer process.[3] In the acridane-porphyrin system, instead, the porphyrin moiety retains its emission, since no electron transfer occurs between the two units. On the other hand, an efficient energy transfer process from the acridane unit to the porphyrin component has been observed upon acridane excitation. Interestingly, the switching between the acridinium/acridane forms allows the tuning of the photophysical properties of the arrays.

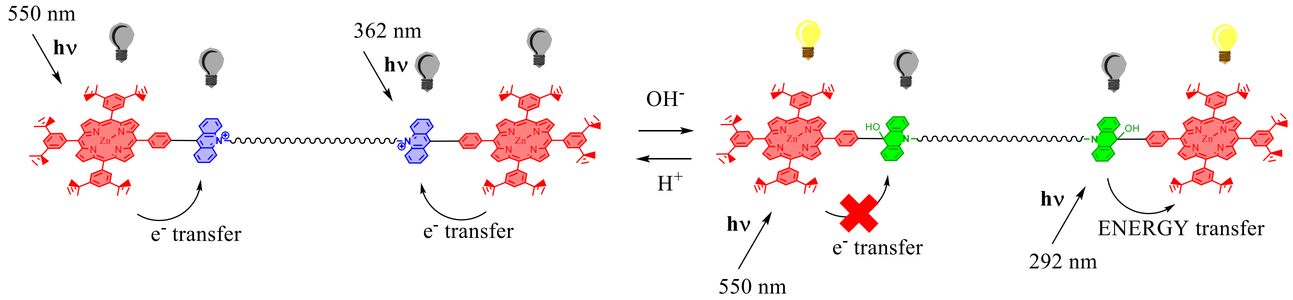

Fig. 1. Scheme of the photophysical behaviour of the two conjugates.

Aknowledgments:
The work is supported by the H2020-MSCA-ITN-2017-765297 project "NOAH" and by the H2020-LC-SC3-2020-RES-RIA-101006839 project "CONDOR". Special thanks go to the Italian CNR (PHEEL project).

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Flash-F18

Charge transfer dynamics in nanostructured wo_3 and wo_3/$bivo_4$ photoanodes

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The production of hydrogen from the water splitting using solar energy is a key goal of photoelectrochemistry, since solar is one of the most appealing and widely distributed energy sources.

Metal oxides such as WO_3 and $BiVO_4$ are good candidate photoanodes for water oxidation. $BiVO_4$, is a semiconductor that can be prepared in a nano-structured form with interesting spectral absorption characteristics (E_{gap} ca. 2.5 eV) and values of the valence and conduction bands that make it suitable for applications in photo electrolysis for the production of solar hydrogen [1]. Unfortunately, the low mobility of the charge carriers and the less than ideal stability under polarization and illumination conditions preclude its effective use as a single junction. The formation of n-n junctions on porous materials such as WO_3 is a promising approach to solve the problem of poor mobility of $BiVO_4$ carriers. Efficient charge separation in the n-n junction still requires additional positive potential to counter carrier recombination. A common approach to reduce the need for such strong positive potential is the exploitation of an electrocatalyst on the surface of the photoanode to acts as a hole transfer medium, contributing to decouple electrons and holes. Cobalt hexacyanoferrate, the cobalt−iron analogue of Prussian blue (CoFe-PB), is a robust, effective, and inexpensive water oxidation electrocatalyst. CoFe-PB modification of $WO_3/BiVO_4$ photoanodes produces substantial improvements in both the onset potential and stability in neutral conditions. [2] In order to obtain kinetic information on the mechanisms of electron and hole recombination and transport, transient absorption spectroscopy (TAS) was used, on a time scale ranging from 10^{-4} to 1s, under polarisation. The role of the catalyst is supposed to be to accelerate the kinetics of water oxidation by decreasing the lifetime of the hole in the CoFePB-modified n-n junction, but no such effect was observed, at least in the time window explored, rather an increase in the lifetime was detected.

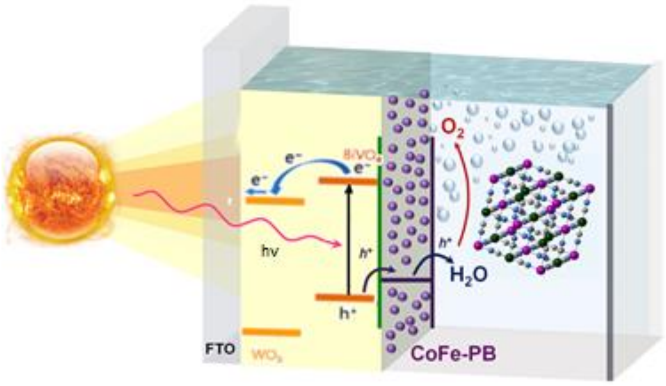

Fig 1. Schematic representation of water oxidation process using $WO_3/BiVO_4$/CoFe-BP

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Flash-F19

Planar and nanostructured $WO_3/BiVO_4$ heterojunction photoanodes: effects of the morphology on the photoelectrochemical performance

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Water splitting using solar energy in the presence of a heterogeneous photocatalyst has long been studied as a potential alternative to obtain clean, energy-rich fuels such as H_2. Among the most studied materials to be employed in the field of photoelectrocatalysis (PEC), tungsten trioxide (WO_3) and bismuth vanadate ($BiVO_4$) have emerged as the most promising photoanodes to drive the water oxidation reaction, the kinetic bottleneck of the overall water splitting. In particular, when these two materials are combined in a heterojunction, a synergistic effect is obtained, due to the formation of a heterostructure with an extended visible light harvesting capability and an increased separation of the photoproduced charges [1]. Moreover, controlling the morphology of the photoelectrodes is another extensively employed strategy that can bring to beneficial effects on their PEC performance. In this work, a nanostructured WO_3 photoanode with a nanoflake-like (NF) morphology has been prepared. A thin layer of $BiVO_4$ was then deposited on the WO_3_NF to obtain a WO_3-$BiVO_4$ composite. At the same time, WO_3 and WO_3-$BiVO_4$ electrodes displaying a planar morphology and comparable tungsten oxide thickness were also prepared, in order to investigate the effects of WO_3 morphology on the PEC performance of the photoanodes. Incident Photon to Current Efficiency (IPCE) analyses (Fig. 1) evidence that the flat heterojunction exhibits low PEC efficiency below 420 nm, which progressively decreases to a null IPCE value around 350 nm, due to the activation of a detrimental recombination path [2]. The nanostructured heterojunction, on the other hand, presents growing efficiencies in the UV range and overall higher IPCE values also under visible light, overcoming the limitations of the planar composite with an enhanced separation efficiency in the photoelectrode bulk.

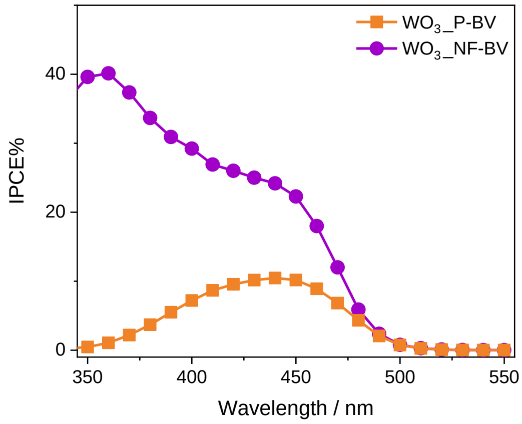

Fig. 1. IPCE% of WO_3_P–BV and WO_3_NF–BV in 0.5 M Na_2SO_4 at the fixed potential of 1.23 V vs RHE in back-side configuration.

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Flash-F20

Laser induced impulse generation on polymers for space propulsion applications

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The well known phenomenon of laser ablation recently attracted interest also in space applications as possible propulsion technique for micro and nano satellites, whose number in earth orbit is rapidly increasing.

During laser ablation a small quantity of mass leaves the irradiated surface with very high exhaust velocity, so that a recoil impulse of the order of μN s is generated on the target material. In order to exploit this potential application of laser ablation, it becomes of fundamental importance the understanding of the laser-material interaction as well as the mechanisms underlying the impulse generation process, so that optimized fuel materials can be designed.

Polymers are generally considered to be good candidates as fuel materials, with respect to metals, thanks to their lower mass density and lower ablation threshold. Among commercially available polymers poly(vinyl chloride) (PVC) shows interesting impulse generation performances [1]. However because of its low absorption it also owns poor ablation properties. A commonly used technique consists then in doping it with an absorber, that can be another polymer, a dye molecule, or nanoparticles. For example, carbon nanoparticles (CNP) are reported as absorbers that help initiate thermal decomposition of the polymer.

In this work impulse generated by PVC doped with CNP and by PVC blended with poly(styrene-sulfonate) (PSS) is compared, by measuring it with a specifically designed ballistic pendulum [2]. Laser generated impulse is significantly enhanced by increasing the optical absorption of the target material. Moreover, optical and thermodynamical characterizations show that the localized absorption of laser radiation by CNP results in a more efficient laser-material interaction for the generation of a mechanical impulse [3].

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Flash-F21

Photon Up-Conversion Sensitized by Semiconductor Nanocrystals

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The upsurge of solar cell efficiencies is becoming increasingly challenging in the last decade; one promising strategy to overcome the Shockley–Queisser limit is the Photon Up-Conversion via Triplet-Triplet Annihilation (TTA-UC), that is a bimolecular process converting lower-energy photons into higher-energy photons. [1]
The discovery of UC in the 1960s involved an organic pair as sensitizer and annihilator, limiting the spectral absorption range and consequently the upconverted emission wavelengths. The introduction of hybrid system has been a turning point for UC, in fact with semiconductor nanocrystals as sensitizer we are able to tune the absorption band of the nanomaterials from VIS to near-infrared (NIR) modifying their composition, dimension and shape. [2] The interest of this versatile mechanism is on the Near Infrared-to-Visible conversion leaving room to new classes of applications such as infrared sensitization of silicon solar cells and the fabrication of low-cost infrared sensing cameras. [3,4] Moreover, since NIR photons are weakly absorbed in aqueous environments, NIR-to-visible UC bears promise in biological probing. [5]
In this work we want to exploit the strong and broad-band light absorption of nanocrystals adopting them as triplet sensitizer and combining them with a transmitter ligand to transfer the energy to an organic molecule used as annihilator (Figure 1). In particular, we deal with nanocrystals with different composition (CdSe and PbS quantum dots) in order to achieve green-to-blue and NIR-to-yellow UC respectively.

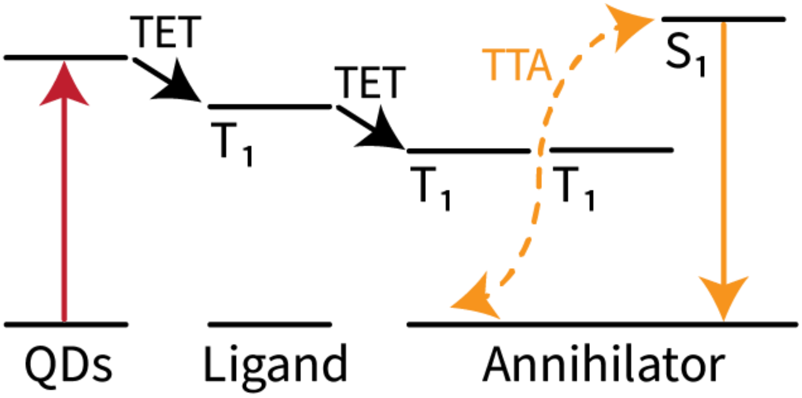

Fig. 1. Up-Conversion mechanism using nanocrystals as sensitizer, transmitter ligand to passivate the crystal surface and transfer the energy to the organic molecule employed as annihilator.

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Flash-F22

Molecular sensitizers for photo-3d printing of ceramic components

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In recent years there's been a growing interest in additive manufacturing and 3D printing. These techniques can be applied to different technological fields and, in particular, they can be proposed as one of the possible solutions to ceramic materials' processing. Ceramics are characterized by high hardness, chemical stability and high-temperature resistance. They are also biocompatible and suitable for the realization of different kind of implants, prostheses and biomedical devices. [1]

Through the application of additive manufacturing technologies to ceramic materials, it is possible to obtain three-dimensional structures with high degree of accuracy and high surface finish, that couldn't be obtained otherwise with conventional machining.

In this work we have studied particular compositions of photopolymeric resins added with ceramic powders, which can be used in the 3D printing technique known as Digital Light Processing, suitable for the manufacturing of complex geometry products with high degree of detail. [2]

The term '3D printing' indicates the building up process of three-dimensional structures from a digital file. The object is created by laying down successive layers of material in order to obtain a complete solid. The technique we employed is called vat polymerization, that involves a photopolymerization of a liquid monomeric resin. We have selected three different visible light absorbers (sensitizers), acting as photoinitiators towards photopolymerization. [3]

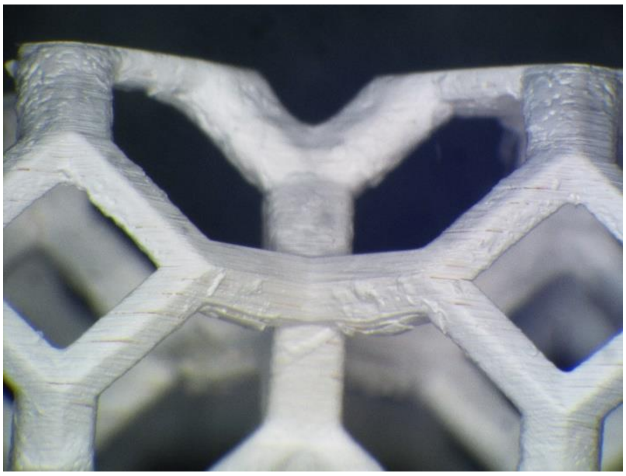

Figure 1 3D printed ceramic object based on zirconia and yttria, obtained by vat polymerization triggered by visible light.

After gaining mechanistic information about the electron transfer events which trigger visible light photopolymerization, we have formulated resins that were tested and validated in the 3D printing process of ceramic materials.

This work has demonstrated the pivotal role of the sensitizers in determining the rate of the photolopymerization that is a critical parameter for achieving a good precision and definition in the photo-3D printing of ceramic objects with complex geometry. This process could be further optimized through some modifications of the molecular structure of common organic sensitizers, allowing to reach higher quality in the production of ceramic objects for biomedical applications.

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Flash-F23

Investigation of Energy Transfer: fluorescent material as a bridge to persistent luminescence

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Persistent luminescence (PersL) is the optical phenomenon in which luminescence lasts for seconds or even days after ceasing excitation (afterglow effect). This effect is due to the crystal defects present in solid phosphors. Under excitation, the generation of charge carriers takes place and subsequently they are trapped by defects, but when the excitation ceases, the trapped charge carriers can escape from the defects and recombine to generate the PersL[1]. The PersL offers exciting opportunities for different application like in vivo imaging, optical data storage or unconventional light generation. In general, tuning and regulating the defects can lead to a control of the optical properties, including the intensity, decay time and emission wavelength; the so-called defect engineering is used to find the balance between large storage capacity, persistent luminescence kinetics and emission efficiency [2]. However, luminescence intensities in many cases is still a challenge. We utilize fluorescent material as a way to control and regulate the different aspects of Persistent Luminescence, above all intensities and the decay times. So zinc sulfide nanoparticles (ZnS) have been synthesized and mixed with commercial solid phosphor powders (CaS:Eu, $SrAl_2O_4$ Eu^{2+}, Dy^{+3}) to investigate the impact of energy transfer processes on the overall luminescence behaviour.

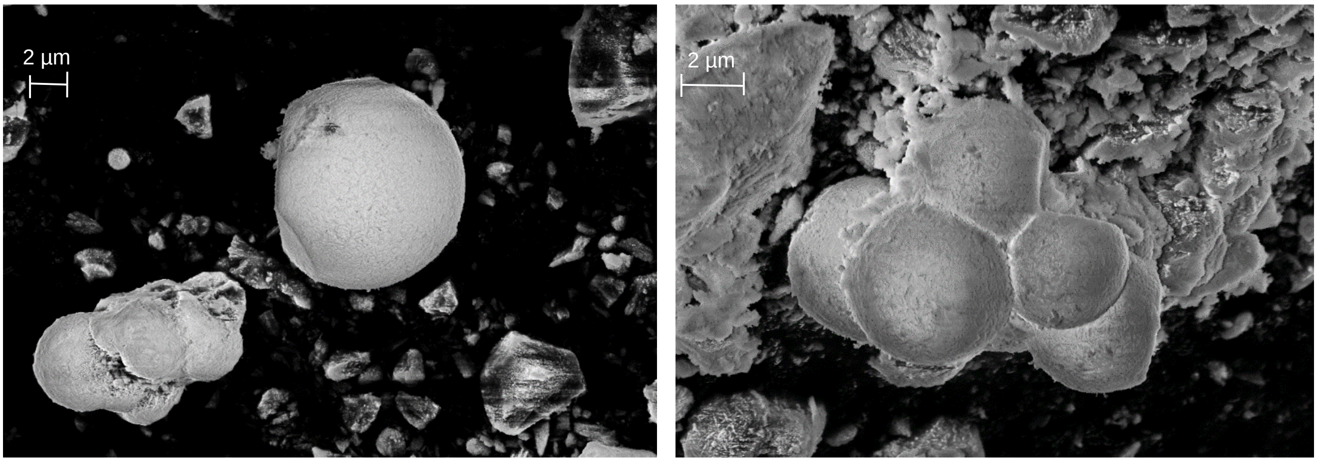

Fig. 1. SEM images of ZnS nanoparticles.

These materials have been fully optical characterized (emission and absorption spectra, gated spectra and kinetics) and also measurements regarding the environmental behaviour will be presented and discussed.

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Flash-F24

Neutral and Cationic Luminescent Iridium Complexes: synthesis and their application in electrochemiluminescence

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The current developments of optoelectronics and bionanoscience take great advantage from the ability of organic, organometallic and hybrid compounds to fulfill specific needs and requirements. Phosphorescent transition-metal complexes, in particular octahedral iridium(III) ones, have been the target of intense researches given their high stability and excellent photophysical properties, such as high luminescence quantum efficiency and short radiative lifetime; in addition, they can be easily engineered in order to judiciously tune their emission colour, electronic energy levels, charge transfer behaviour and steric hindrance.[1] Iridium complexes are becoming successful emitters in many technological fields other than OLEDs. Electrochemiluminescence (ECL) applications are looking at the use of these complexes as alternatives to the ruthenium(II)polypyridine complexes.[1] for their reversible electrochemistry and color tuning

In this contribution, we will present the synthesis of a family of cyclometalated heteroleptic Ir(III) complexes with emission centered in the blue, green and nearIR spectral regions (Figure 1). [2,3] Their optical properties will be discussed in correlation to their neutral or cationic nature and preliminary ECL studies shown. Further, bioconjugation strategies will be highlighted in the development of an efficient tools for bioimaging and clinical diagnostics with nearIR electrochemiluminescence.

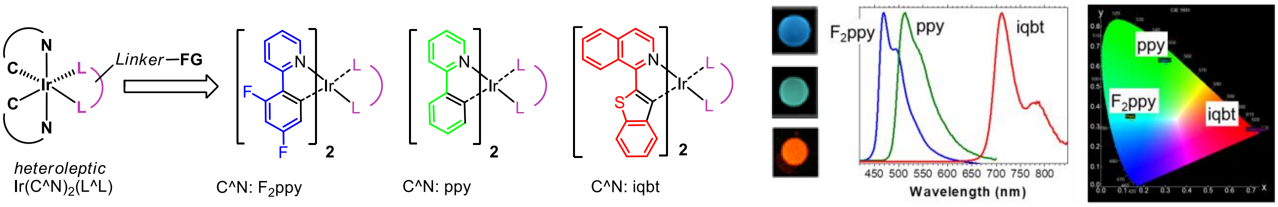

Fig. 1. General structure of the studied heteroleptic Ir(III) complexes and their corresponding phosphorescence emission.

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Poster-P1

The effect of size and bioconjugation functionalities on the luminescence emission of ru(bpy)$_3^{2+}$ doped silica nanoparticles

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Luminescence-based techniques are powerful tools in biological sensing and imaging, because of their sensitivity and versatility.[1] In this field, great attention has been given to the development of luminescent nanomaterials that have been used for many purposes like temperature sensors, lasers, solar cells, biosensors, biological probes and drug delivery. It is well known that the luminescence emission intensities of the luminescent nanomaterials depend on many factors such as the type, shape and size of the nanomaterials.[2] Among all these nanomaterials, dye-doped silica nanoparticles (DDSNs) are versatile systems because of their versatility, brightness and quite simple fabrication procedures.[3] Size is one key parameter affecting the behaviour of DDSNs in most of the environments, with strong effects on brightness and on the photophysical properties of the luminescent molecules embedded in the silica matrix.[4,5] In our case, we have tried to develop DDSNs and to study their photophysical and electrochemiluminescence (ECL) properties. ECL is the process whereby redox-active species generated at electrode surfaces undergo electron transfer reactions to form excited states that emit light without the need for an external light source and has remarkable feature such as wide dynamic range, high sensitivity, low background signal, low cost, good temporal and spatial controllability, simplicity and rapidity.[6,7]

In this work, we have synthesized monodispersed and spherical [Ru(bpy)$_3$]$^{2+}$ DDSNPs with different sizes (from 30 to 150 nm) following a reverse microemulsion method. The surface of these DDSNPs was functionalized with amino and carboxyl groups to prevent aggregation and enable bioconjugation. From the study of the photophysical properties of these DDSNPs, their phosphorescence quantum yields and lifetimes are found to be greater than that of the corresponding free [Ru(bpy)$_3$]$^{2+}$ complex. Moreover, their ECL emission intensities are enhanced compared to that of the free [Ru(bpy)$_3$]$^{2+}$. In our investigation, we have confirmed that the size of the DDSNPs is a crucial factor that affects both photophysical and ECL properties. Therefore, these results are valuable insight for the fabrication of ECL nano labels based on DDSNPs.

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Poster-P2

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

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

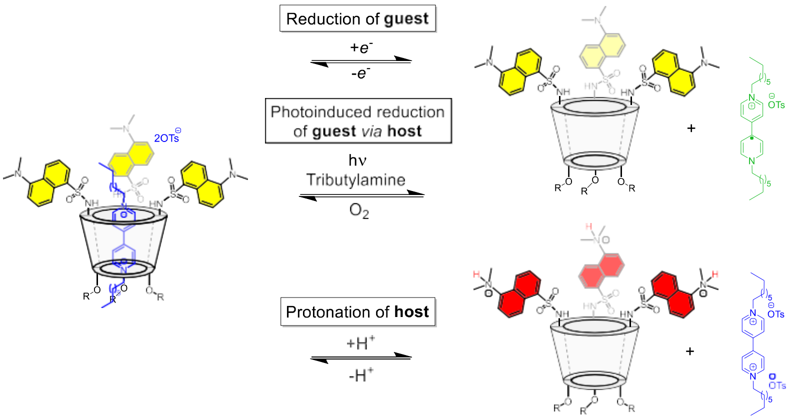

Fig. 1. Schematic representation of the calix[6]arene-based pseudorotaxane and its responsiveness to different stimuli.

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Poster-P3

Squaraine Dyes as Fluorescent Turn-on Probes for Proteins

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Mucins are a family of long polymeric glycoproteins which can be overexpressed in several types of cancers, and over recent years, great attention was addressed to identify mucins as an important biomarker of adverse prognosis. Fluorometric detection mediated by fluorescent probes could represent a winning strategy in the early diagnosis of different pathologies. Among promising biological fluorescent probes, squaraines are gaining particular attention, thanks to their sharp and intense absorption and emission in the NIR region.[1] In this contribution, three squaraine dyes bearing different substituents and with different lipophilicity have been investigated for their ability to detect mucin. The turn-on response upon the addition of mucin has been investigated by means of absorbance and fluorescence spectroscopy. After a preliminary screening, the squaraine bearing bromine as a substituent and C4 aliphatic chains (Fig. 1) showed the highest fluorescence turn-on and highest affinity for mucin than albumin.[2] To further highlight the selectivity of this squaraine for mucin, the fluorescence response has been evaluated in the presence of serum and site-specific proteins different than albumin. Absorption spectroscopy was used to characterize the binding mechanism of squaraine to mucin.

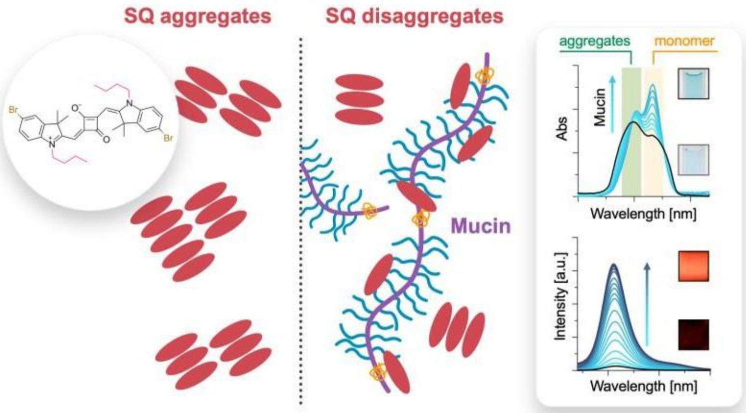

Fig. 1. Mucin induces disaggregation of squaraine aggregates.

The project leading to these results has received funding from the European Union's Horizon 2020 research and innovation FET-OPEN under grant agreement ARTIBLED No. 863170.

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Poster-P4

Multichromophoric coordination polymer containing luminescent lanthanide centers for white light emitting optoelectronic devices

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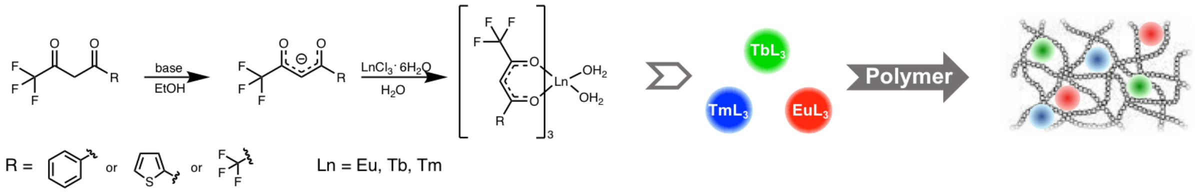
The production of white or panchromatic light is based on the generation and the intensity control of the three fundamental (red, green and blue) or two complementary (e.g., turquoise and orange) colors in order to cover the whole visible range from 400 to 700 nm. The goal is usually achieved using different red, green and blue independently emitting small molecules. The major drawback of this strategy is the different stabilities of the emitters that reduces or changes the performances of the light emitting device over its lifetime. The use of a single molecule bearing two or more color centers will straightforwardly overcome the stability issue of the independent emitters, as they are now part of the same moiety. Light emitting lanthanide complexes are attractive for this kind of application as their emission generates from metal centered excited states which are only slightly affected by the coordination environment. Here, we propose an original strategy to realize new polychromic light emitting materials for the preparation of organic optoelectronic devices, based on a single organic polymer coordinating a suitable amounts of red, green and blue phosphorescent lanthanide complexes, displaying a continuous gamut of color coordinates.



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Poster-P5

Transparent and Colorless Dye-Sensitized Solar Cells using Polymethine Dyes

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Enhancing the performances, stability and aesthetics of transparent photovoltaic (TPV) is crucial for the development of integrated PV in windows. Among the different possible approaches, Dye-sensitized Solar Cells offer a unique sustainable choice for transparent and even colorless windows, thanks to their wide versatility in the choice of dyes, electrolytes and redox couples as well as their ability to use diffuse light and work in low-light conditions. [1]

The photosensitizer plays a crucial role in a non-intrusive wavelength-selective NIR-DSSC system. Until now, different families of NIR chromophores have been investigated with relatively low success in terms of transparency and power conversion efficiency. Recently, thanks to the joint efforts of different research groups within the IMPRESSIVE project (https://impressive-h2020.eu/), we proposed a fully transparent and colorless DSSC. [2]

Starting from this result, innovative strategies have been applied (on both dyes and electrolytes) finally obtaining a never-reached aesthetic level, up to 80 % average visible transmittance (AVT), with a color rendering index (CRI) of 96 where color coordinates approaching the white point.

Acknowledgement:

This project has received funding from the European Union's Horizon 2020 research and innovation program under Grand Agreement n° 826013.

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Poster-P6

C-dots as photoorganocatalysts for synthesis under metal free conditions

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Carbon-dots (CDs) are highly emissive nanomaterials that can be prepared through a hydrothermal bottom-up approach from renewable sources such as fructose, citric acid, glucose, and organic wastes [1], thus playing a promising role in the conversion and valorization of organic waste. The proprieties of CDs (dimension, shape, emission, quantum yield) depends on both starting substrates and reaction conditions [2].In this work we investigated the photophysics and photochemical behavior of different CDs, in order to assets them as organic photocatalyst for Atom Transfer Radical Addition processes [3]. For this aim CDs with different precursor, shape and dopants were tested as photoorganocatalyst (POCs) in the 1,2-functionalization of olefins with various alkyl halides. Due to their interesting applications as POCs and their inexpensive and simple synthesis starting from easily available carbon-based materials, these preliminary results pointed out the potentialities of CDs in photoredox catalysis under metal-free conditions.

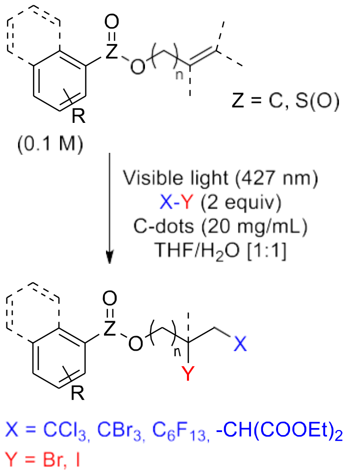

Fig. 1. Reaction scheme

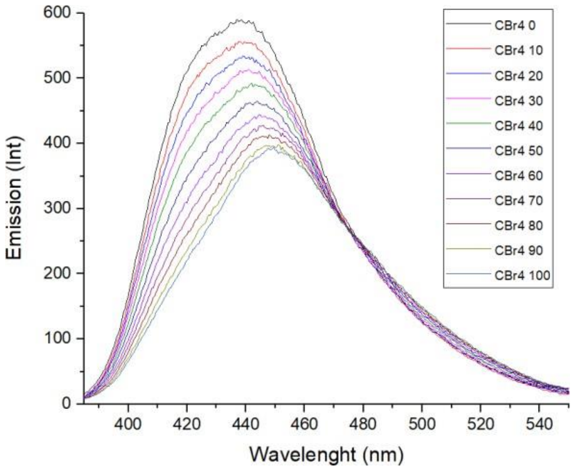

Fig. 2. Quenching of CDs excited states

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Poster-P7

Organic and Organometallic Photoactive Molecules: versatile materials for Vis-NIR optoelectronics and biological probes

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Photoactive organic-based molecular materials hold a great deal of potentials in many technological and biomedical fields. In this respect, we have undertaken researches exploiting two classes of materials, namely luminescent cyclometalated Iridium complexes[1] and Porphycenes [2] (Fig.1).

Iridium complexes, owning to their versatility in chemical design and, accordingly, broadly tuneable phosphorescence, have been longed studied in our group for different applications. In this contribution, we present our recent results on: (i) a new strategy to obtain Ir(III) complexes, carrying a single emissive ligand, as efficient near-infrared (NIR) emitters in fully-evaporated OLEDs;[2] (ii) the use of neutral and cationic heteroleptic systems as electrochemiluminescence (ECL) luminophores with complementary emission in the blue, green and NIR spectral regions and (iii) the development of theranostic Ir(III) complexes as imaging and therapy agents, simultaneously.

Porphycenes (**H_2Po**), tetrapyrrolic 18π electrons chromophores that are constitutional isomers of the porphyrins,[3] are currently studied as ultrafast responsive materials with intriguing tautomeric activity. We report here the first study on H_2Po continuous and compact 2D and 3D vacuum deposited thin films, studied by means of UV-Vis-NIR absorption and emission spectroscopies, surface differential reflectivity (SDR) and reflectance anisotropy spectroscopy (RAS), in conjunction with surface microscopy (AFM).[4]

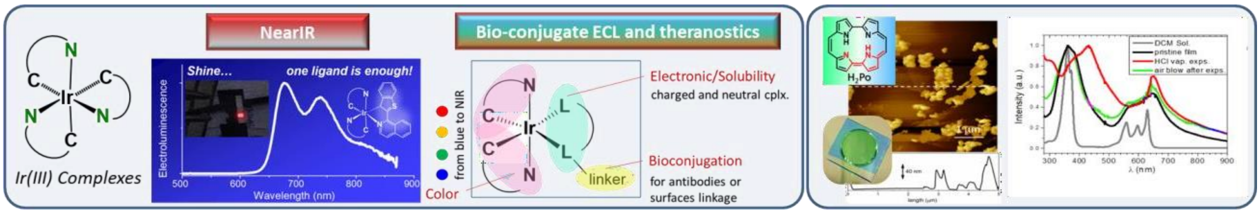

Fig. 1. *left,* studied Ir complex from molecules to applications; *right*, **H_2Po** AFM topography and Uv-Vis spectra in solution and thin film during blue-to-green acidochromic sensing (inset).

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Poster-P8

Intrinsic fluorescence of human neuroglobin

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Human neuroglobin (hNgb) is a recently identified globin containing a six-coordinated heme b. It is mainly expressed in the neurons of the hypothalamus and in the retinal cells, whereas it is present at a relatively low concentration in other parts of the central nervous system and in non-neuronal tissues. Although the physiological role of hNgb has not completely understood, a neuroprotective role against hypoxic/ischemic and oxidative stress has been suggested [1]. Strong evidence has been gained that in vivo hNgb is overexpressed under mitochondrial dysfunctions and neurodegenerative disorders, such as Alzheimer's disease [1].

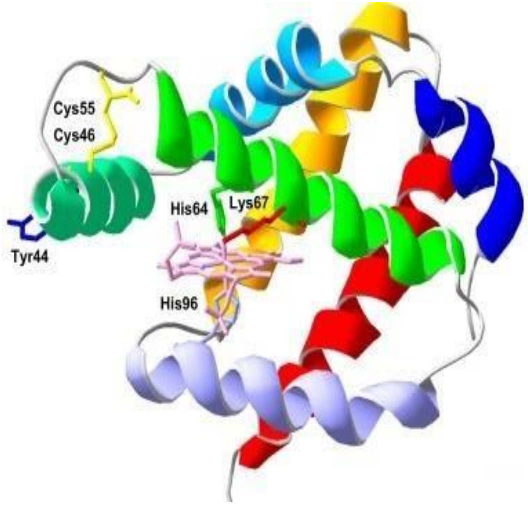

Fig 1. Structure of human neuroglobin. In pink the heme group.

The intrinsic fluorescence of proteins provides an important tool to study their structure and conformational transitions, thanks to the high sensitivity of fluorescence properties of tryptophan residues to the local environment. Here we report the study, based on steady-state and time resolved fluorescence measurements, of conformational changes of hNgb induced by urea, a chaotropic agent, and by sodium dodecyl sulfate, which is able to simulate the interaction of proteins with phospholipids in the cell membranes. The emission spectra, fluorescence lifetimes and fluorescence anisotropy provide important information on conformational changes in hNgb.

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Poster-P9

Supramolecular-based fluorescent ligands as sensing tools for the detection of nonsteroidal anti-inflammatory drugs

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Tackling the problem of pollution is crucial for the wellbeing of our planet. Among the substances posing a risk for the environment, the class of nonsteroidal anti-inflamatory drugs (NSAIDs) is one of the most in need of being addressed.[1] One of the challenges correlated to this class of pollutants is their detection and quantification, mainly because traditional analytical techniques, such as HPLC or GC are the only proven methods for the detection of EPs but they require time and qualified personnel. One of the more promising strategies of dealing with the detection of pollutants is optical sensing using luminescent chemosensors, a technique which has proved to be efficient to overcome the limitations of traditional analytical techniques ensuring a quick, cost-effective real time analysis of samples.[2]

In this work we report the complete photophysical characterization of a set of supramolecular fluorescent chemosensors, developed for the detection of NSAIDs. These macrocyclic and pseudomacrocyclic probes are based on squaramides moieties which give the sensors strong hydrogen bond donors, and a dansyl fluorogenic unit for signal transduction; the sensors are designed with multiple binding sites to improve affinity and selectivity towards target analytes, and to reduce the interference of inorganic ions that can be found in real matrices.

All the probes were capable of complexing ketoprofen at micromolar concentrations in acetonitrile, via H-bonds and hydrophobic interactions, resulting in a quenching of the fluorescence and a shortening of the fluorescence lifetimes. In addition, competition studies were performed to assess specificity and selectivity of the probes. This work is a thus a step toward the development of chemosensors arrays for the detection of NSAIDs.

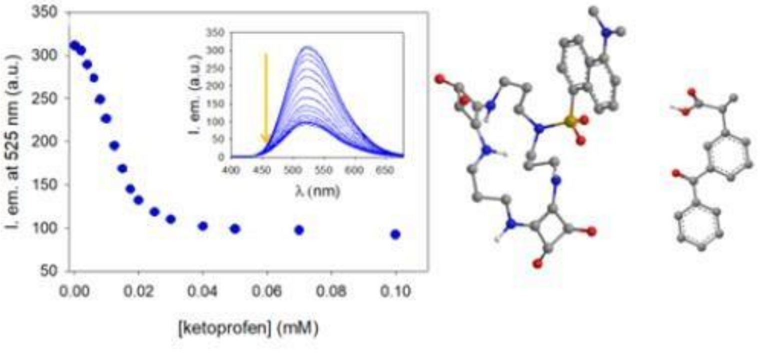

Fig. 1 Trend of emission at maxima versus concentration of ketoprofen of one of the investigated probe (left) and emission spectra upon addition of increasing amont of ketoprofen (inset); 3D structures of the probe and ketoprofen (right).

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Poster-P10

Decatungstate photocatalyzed synthesis of unnatural aminoacids via radical functionalization of α-imino esters

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α-Imino esters are versatile building blocks for diverse synthetic applications, spanning from natural products preparation to pharmaceutical research. Interestingly, these derivatives offer a straightforward access to a variety of unnatural α-amino acids. [1] Apart from simple α-imino esters (**I**), α-oximino esters (**II**) and α-hydrazono esters (**III**) are important additional members of the same family (Figure 1, left part). Their typical reactivity is represented by the nucleophilic addition of organometallics or active methylene compounds, the preferred functionalization site being the C-atom of the imine functionality. Other elaboration strategies of this building block include metal-catalyzed additions, the (asymmetric) hydrogenation of the C=N and/or C=O double bonds, as well as different pericyclic processes. [1]

Herein we present a radical methodology for the photocatalyzed hydroalkylation of α-imino esters via HAT (hydrogen atom transfer). [2] This strategy is based on the use of a polyoxometalate, tetrabutylammonium decatungstate (TBADT, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$), as the photocatalyst. Upon absorption of a photon, this compound is able to cleave homolytically (often with high chemo- and regioselectivity) the C–H bond in a variety of organic derivatives. [3] After assessing the excellent performance of α-hydrazono esters (**2**) as radical traps, we used them to intercept radicals (**1**$^\bullet$) photogenerated from oxygenated derivatives, aldehydes and cycloalkanes (**1**; see R-H in the right part of Figure 1) to finally deliver unnatural α-aminoacid derivatives of general formula **4**.

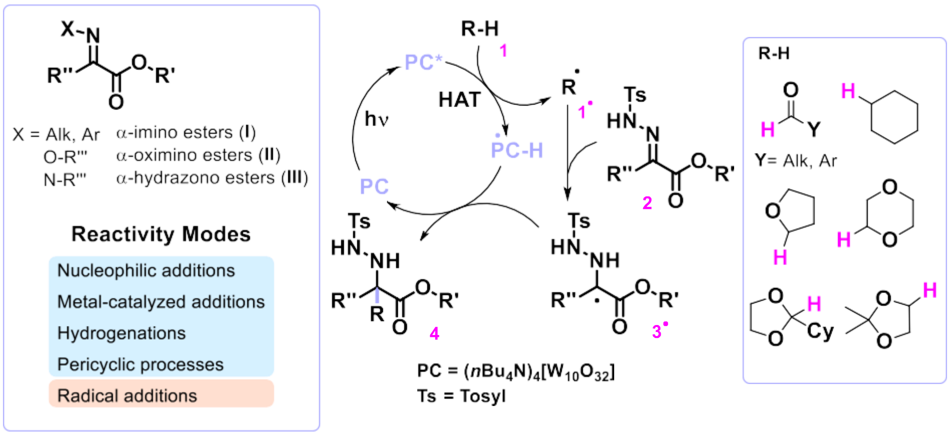

Fig 1. The chemical scaffold characteristic of the α-imino esters family along with their typical reactivity modes: well-established methodologies are highlighted in blue, currently underdeveloped strategies in red (left). Mechanism of the hydrogen atom transfer (HAT) process for the functionalization of α-hydrazono esters developed in this work and molecules used as hydrogen donors (R-H, right).

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Poster-P11

Fluorescent NO photodonors as phototheranostic agents for neurodegenerative diseases

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The aggregation of amyloid proteins is involved in several illnesses, including neurodegenerative ones such as Alzheimer's and Parkinson's diseases [1]. The detection of early-stage amyloid fibrils as well as the capacity to delay fibrils formation are extremely important for an early diagnosis and therapy. While the fluorophore thioflavin T (ThT) has been extensively used in amyloid aggregates detection, it has been recently understood that it lacks of specificity and, mostly, cannot always detect fibrils at a very early-stage. Among alternatives, dipyridamole, for instance, has been recently demonstrated to be more sensitive than ThT to the early-stage aggregation of amyloidogenic proteins [2]. In parallel, other fluorescent probes, such as dyes derivatives, transition metal complexes, nanoparticles are gaining increasing interest for the detection of early-stage amyloid fibrils. In this scenario, a phototheranostic platform able to integrate both the diagnostic and therapeutic functions under the input of light stimuli is very challenging. Recently it has been reported that a loss of nitric oxide (NO) signaling contributes to the dysregulation of cerebral blood flow in Alzheimer's disease (AD) and that NO levels are usually reduced in AD. Moreover, the nitration of the tyrosine residue of amyloid β reduces its aggregation suggesting that NO might have an important role in preventing AD [3]. Here, we present fluorescent NO photodonors (NOPD) as phototheranostic agents for the detection of early-stage amyloid aggregates and the NO-based phototherapy of amyloid related illnesses. The interaction of these NOPD with different amyloidogenic proteins has been investigated in order to follow their aggregation and, at the same time, to shed light on the influence of the photoreleased NO on the aggregation phenomena.

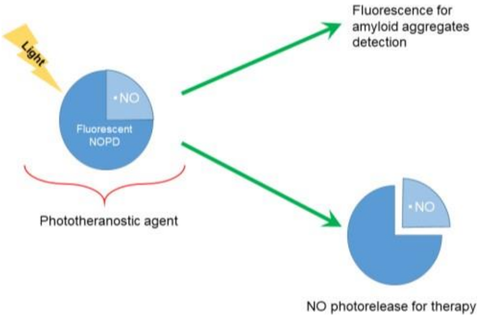

Fig. 1. Schematic representation of the fluorescent NO photodonor (NOPD) for phototheranostic.

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Poster-P12

Prediction on Carbanions Reactivity with Carbon Dioxide: Application to the Electrochemical Carboxylation of α,β-Unsaturated Ketones

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The vision of CO_2 as a C1-building block is related to the electrophilicity of the C atom that can be employed as the centre for the creation of new C-C bonds with nucleophilic organic partners[1]. The thermodynamic and kinetic barrier of the activation of CO_2 can be overcame upon enhancing the reactivity of the organic partners, for example, involving electrochemical or photochemical reduction to form carbanions C−, being sufficiently reactive toward the addition of CO_2. Nevertheless, a rational approach to describe and predict the reactivity of such species is still missing[2], and in some cases the nature of the reactive species towards CO_2 is elusive.

In this work, we develop a predictive model to elucidate the reactivity and mechanics of carboxylation of organic substrates[3] by establishing a linear correlation of the standard free energy (ΔG^0) of the carboxylation reaction with the basicity of the carbanion C−, expressed as the pK_a of the CH/C− couple. We identify a threshold value of pK_a (ca 36 in CH_3CN) for the CH/C− couple, that determine the exo or endoergonic nature of the carboxylation reaction.

We then match the predictive model with the experimental electrochemical carboxylation of flavone and chalcone as model compounds of α,β-unsaturated carbonyl scaffolds, showing significant biological interest[4], [5]. In both cases, carboxylation occurs in the β-position from the doubly reduced dianion intermediates (calculated ΔG^0 of carboxylation in $\beta < -12.8$ $Kcalmol^{-1}$, associated with pK_a values for the conjugate acids > 50.6). Conversely, the one-electron reduced radical anions are not reactive toward carboxylation ($\Delta G^0 > +20$ $Kcalmol^{-1}$, in either α or β position, consistent with pK_a of the conjugate acids < 18.5).

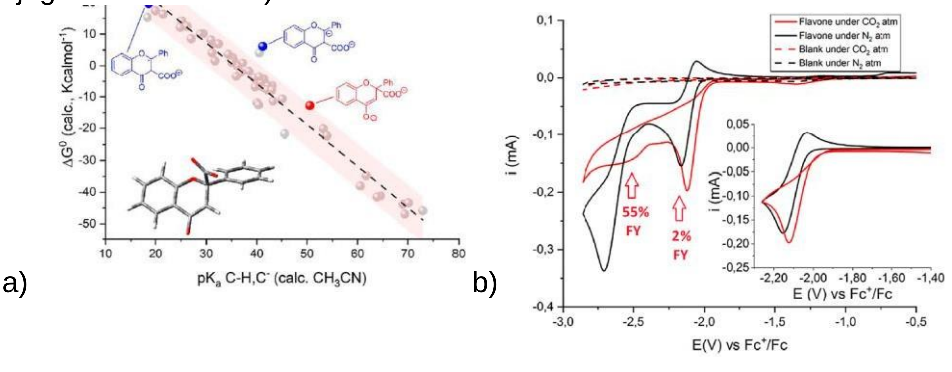

Fig. 1. a) Predictive model applied to flavone derivatives upon carboxylation. **b)** Cyclic voltammetries of flavone with the relative faradic yields (FY) of the electrochemical carboxylation process, giving β-flavanone-2-carboxylic acid methyl ester as the product.

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Poster-P13

Indium-modified Copper nanocubes for syngas production from aqueous CO_2 electroreduction

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The level of carbon dioxide in the atmosphere is constantly growing mainly due to anthropogenic activities causing the well known greenhouse effect that represent one of the greatest challenges to contemporary society. On this regard electroreduction of CO_2 represents an appealing strategy to rethink a waste and an environmentally dangerous product as an innovative feedstock for the formation of value-added carbon neutral compounds. Among the metal electrodes able to catalyze such process, copper plays a central role [1]. Strategies aimed at tuning Cu selectivity comprise nanostructuring and alloying with heterometals. One of the more investigated nanostructuring strategies consist in the controlled formation of Cu oxides, which then undergo to a re-reduction in CO2R conditions. Several strategies have been reported for the oxidation of Cu foils' surface [2][3][4].

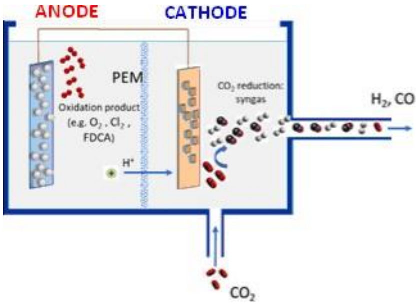

Fig. 1. Scheme of an electrochemical cell for the production of syngas from CO_2

In this contribution, we will report on straightforward electrochemical methods for the formation of Cu-In interfaces. The latter were fully characterized and then used as cathodes for CO_2 electroreduction, leading to the selective production of syngas, whose composition varies upon changing the applied bias and Indium content. Literature examples of copper-indium nanostructured catalysts for CO2R are now still limited.[5]. In particular, the proposed cathode in this work is able to efficiently catalyze gaseous mixtures compatible with the synthesis of methanol or aldehydes (i.e. respectively with 1:2 and 1:1 CO/H_2 ratio) that are produced at a relative low (i.e. -0.62 V vs RHE) applied bias with >4 mA/cm^2 up to 15 mA/cm^2 (i.e. -0.92 V vs RHE) of stable current densities.

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Poster-P14

Effects of matrix and concentration on the photochromism of spirooxazine-doped polymeric films

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One of the strategies to take advantage of the photoswitchable properties of spirooxazines, a well-known class of photochromic dyes [1,2], is represented by their encapsulation in transparent host matrices, like polymers [3], which may induce a variation of the optical properties and improve the performance of the material, thanks to a major protection from oxidative degradation [4].
Herein, we report a study of the modulation of the colourability and the colouring/bleaching rates in different polymeric matrices (Polymethylmetacrylate, PMMA, and expanded polystyrene, PS) of two spirooxazines: 1',3'-dihydro-1',3',3'-trimethylspiro[2H-benz[a]anthra[3,4-b]-1,4-oxazine-2,2'-[2H]indole]-7,12-dione (**SO_1**) and methyl-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]-9′-carboxylate (**SO_2**). The influence of the photochromic concentration and the chemical nature of the polymeric matrix on the photophysical behaviour of the two molecules is investigated.

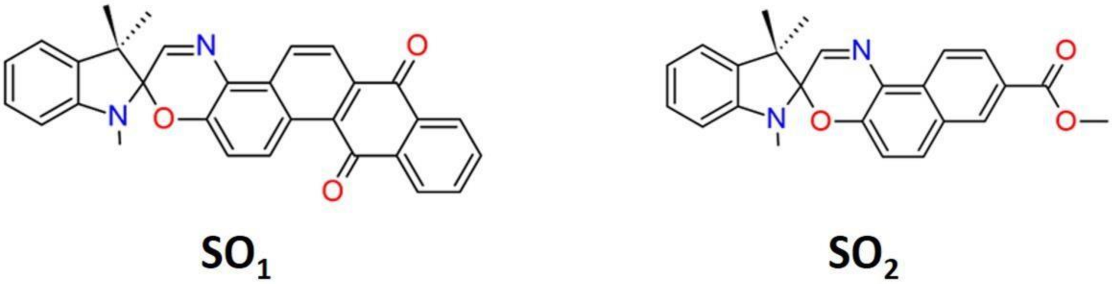

Fig. 1. Molecular structure of the two spirooxazines investigated.

The obtained results show how it is possible to design a multi-purpose photochromic system by simply varying its concentration within the polymeric matrix. Indeed, by the proper choice of the photochromic concentration, thin solid films showing great photoconversion efficiency, with fast change in transmittance, can be achieved under irradiation, together with the possibility to modulate the bleaching rate from few seconds to tens of minutes.

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Poster-P15

Unveiling Inexpensive and Bench Stable Diarylmethylium Salts as Mediator for the Light Induced Hydrosulfonylation of Alkenes

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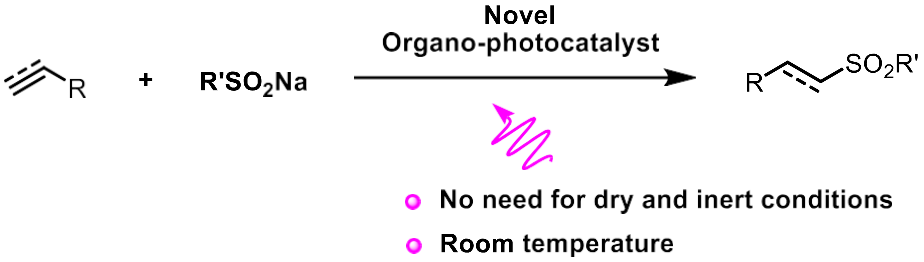
Displaying a plethora of activities, sulfur-based molecules have a pivotal role as functional groups in many natural products, agrochemicals and materials. Above all, they are of particular interest for the pharmaceutical industry [1], with around 284 sulfur-containing drugs approved by the FDA [2]. For these reasons, the development of milder and greener methodologies for the formation of C-S bonds has been the object of intensive work for organic chemists.

Currently in this field, photocatalysis has gained a prominent role allowing peculiar reactivities, barely possible by traditional methodologies [3-4]. As concerns hydrosulfonylation reactions, photocatalyzed methodologies are dominated by Iridium-based complexes, which permit the generation of the sulfonyl radical from different precursors such as sulfinic acids, sulfonyl halides, sulfinates and sulfonyl hydrazides [5]. In this framework, we propose the replacement of expensive Iridium catalysts with novel bench-stable salts. For the first time, diarylmethylium salts are employed as organocatalysts mediating under visible light the formation of the key sulfonyl radical. These salts show high activity at a low catalyst loading and the hydrosulfonylation is feasible at room temperature without the need for dry and inert reaction conditions. High functional groups tolerance and scalability up to 15 mmols are peculiar for this new catalytic system.



- No need for dry and inert conditions
- Room temperature

Fig. 1. Reaction scheme for the organo-photocatalyzed hydrosonylation of alkenes.

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Poster-P16

Properties of new complexes of the type [Cu(6-[quinolin-2-yl-methylen)amino]-2*H*-chromen-2-one)(PP)]PF_6 with bicoordinant diphenylphosphines (PP) with photophysical potentialities

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The investigation of the luminescent properties of transition metal complexes is a very active area of study, due to the increased demand for materials applicable in solar energy conversion and/or light generation processes[1]. Due to their particular structural, photophysical and redox properties, in addition to their abundance and lower cost, Cu(I) complexes are visualized as promising alternatives to these processes compared to other photoluminescent systems based on transition metals[2].

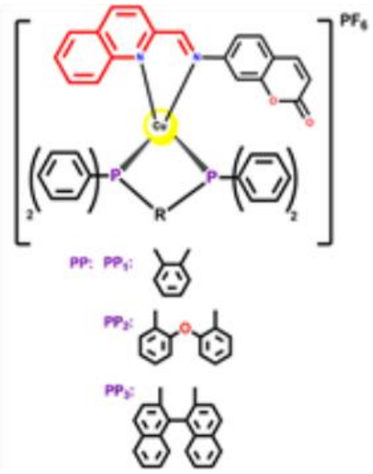

Fig. 1 Complex [Cu(6-[(quinolin-2-yl-methylen)amino]-2H-chromen-2-one)(PP)]PF6. Where, PP1= 1,2-bis(diphenylphosphine)benzene, PP2= bis[2-(diphenylphosphine)phenyl]ether, PP3= (±)2,2'-bis(diphenylphosphine)-1,1'-binaftil).

Under this consideration, three new heteroleptic complexes of Cu(I) were designed and prepared with the NN ligand, which contains quinoline and coumarin fragments, and different PP ligands (**see Figure 1**) which together with contributing to the stabilization of the oxidation state Cu(I), restrict the flattening of the excited state of MLCT endow the compound with low energy □* orbitals[1,2].

The three Cu(I) complexes were obtained using *template* methodology. The structural characterization was performed by the concerted analysis of NMR 1D (^{1}H, ^{31}P, ^{13}C) and 2D (COSY, HSQC, HMBC, HMBC-^{15}N) spectra. The electronic properties, focused on MLCT processes, were established by absorption spectroscopy, UV-visible emission and cyclic voltammetry. The structural and photophysical properties of the three complexes were evaluated in relation to structural differences and geometric distortions.

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Poster-P17

A Proton-Coupled-Electron-Transfer Based Strategy to the Light-Driven Fixation of CO_2

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Over the past decade, photocatalytic redox reactions have emerged as an efficient tool in organic reactions as they use light as the energy source, and through the exchange of electrons they can generate active radical species under mild conditions. Proton-Coupled-Electron-Transfer (PCET) is a redox mechanism that can function as a non-traditional pathway for homolytic bond cleavage so it can play a key role in catalytic reactions.[1] In particular, multi-site proton-coupled electron transfer (MS-PCET) is as a subset of PCET mechanisms where electrons and protons move to (or from) different reagents. This pathway allows the generation of radical species at a more favorable thermodynamic and kinetic cost, while avoiding the formation of high-energy charged intermediates, and the activation barrier of the reaction can slowdown.

We herein present a strategy to use the potential of MS-PCET pathway applied to a redox-neutral photochemical carboxylation process.[2] In particular, this approach is exploited for the generation of benzyl radical species from the electron-rich Hantzsch ester derivate substrate, in the presence of an organic photocatalyst (4CzBnBN) and a base (1,5,7-Triazabucyclo[4.4.0]dec-5-ene,TBD). The beneficial effect of the TBD base is due to an interaction with the Hantzsch ester substrate within H-bonding interaction between the two reagents (Uv-Vis, H-NMR, IR, and Cyclic Voltammetry converging evidence). The hydrogen-bonded complex is then more easily oxidized compared to the HE derivate alone, allowing the generation of a benzyl radical (A) as a key intermediate, subsequently reduced to a carbanion (B), able to react with CO_2. This strategy provides an alternative way to generate the competent intermediates in an overall redox-neutral cycle for the fixation of carbon dioxide.

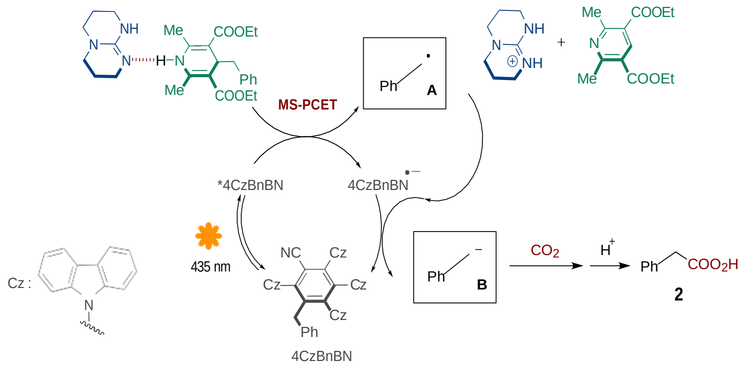

***Fig. 1** Reaction scheme of the redox-neutral photocarboxylation investigated*

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Poster-P18

Photoelectrochemical C-H activation through a quinacridone dye enabling proton-coupled electron transfer

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Photoelectrochemical cells (PECs) constitute an appealing strategy for exploiting solar light to drive sustainable chemical processes, such as the conversion of abundant small molecules and raw materials into valuable products. Since the seminal work by Mallouk et al.,[1] many efforts have been oriented towards the design of dye-sensitized photoelectrodes for the splitting of water into hydrogen and oxygen, combining cathodic water reduction and anodic water oxidation. More recently, oxidation of organic compounds has been considered as an alternative anodic process, [2, 3] with the double advantage of by-passing the significant thermodynamic and kinetic hurdles of the water oxidation reaction, while targeting valuable reaction products instead of oxygen.
In this work, we have developed photoelectrodes based on mesoporous tin oxide sensitized with a quinacridone dye (QNC), employed for the photoelectronchemical oxidation of TEMPO radical and for C-H oxidative activation.

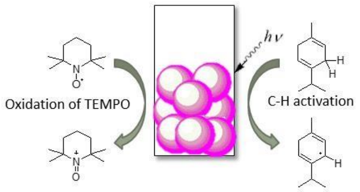

Fig. 1. QNC sensitized photoelectrodes applications.

QNC is a commercially available chemical, has an extended absorption in the visible, is nontoxic and used in inks and paints (pigment violet 19). We performed electrochemical experiments on QNC, which showed that QNC is oxidized through a proton coupled electron transfer process, generating a N centered radical. QNC was then sensitized on semiconductor slides by vacuum evaporation, and the resulting electrodes were characterized through scanning electron microscopy, X-ray photoemission spectroscopy, absorbance spectra, emission spectra and photoelectrochemical tests. These latter demonstrated that QNC sensitized photoelectrodes can be applied to oxidative processes such as the oxidation of alcohols and activation of C-H bonds.

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