



Workshop & NIS Colloquium



Torino, October 6th-7th 2016
Aula Avogadro, Via P. Giuria 7
Department of Chemistry, University of Torino

Organizers: C. Atzori, N. Barbero, C. Barolo, F. Bonino, B. Civalleri, J.G.Vitillo

The workshop is intended to be an informal and a high profile thematic discussion meeting aimed at highlighting the role and potential use of hybrid materials (with porous and non-porous frameworks) in light harvesting and energy transfer. Various exciting topics will be discussed from fundamentals to applications and devices, from host-guest confinement (e.g. dyes encapsulated in porous frameworks) to photo-catalysis, from photoactive therapy to tunable opto-electronic features and solar cells. Contributions will cover both experimental and theoretical viewpoints. The workshop is organized within the frame of NIS Colloquia a series of scientific meetings. The official language of the workshop is English.

Speakers

- Jin-Chong Tan (University of Oxford, UK)
- Frederic Labat (Paristech, FR)
- Sachin Chavan (University of Oslo, NO)
- Enrica Gianotti (UPO, IT)
- Marco Milanese (UPO, IT)
- Alessandra Operamolla (UniBA, IT)
- Claudio Minero (UniTO, Italy)
- Jorge Gascon (TUDelft, NL)
- Ruben D. Costa (FAU-Erlangen, DE)
- Federico Bella (PoliTO, IT)
- Gianmario Martra (UniTO, IT)
- Carlo Nervi (UniTO, IT)
- Giuseppe Paternò (IIT/PolIMI, IT)

PROGRAM

| October 6th, 2016 | | October 7th, 2016 | |
|-------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|--------------------------------------------------------------------------------------------------------------------------------|
| 14:30 | Opening | 9:00-9:45 | Jorge Gascon, TUDelft <i>"Metal Organic Frameworks as potential photocatalysts. Where are we and where are we heading?"</i> |
| 14:45-15:30 | Jin-Chong Tan, University of Oxford <i>"Tailoring Optoelectronic Properties of Host-Guest Metal-Organic Frameworks (MOFs)"</i> | 9:45-10:15 | Alessandra Operamolla, Uni Bari <i>"Drawing from natural materials for organic electronics"</i> |
| 15:30-16:00 | Sachin Chavan, Uni Oslo <i>"Scale up of Zr-based "UiO-66" MOFs"</i> | 10:15-10:45 | Enrica Gianotti, UPO <i>"The therapeutic effect of light: hybrid nanoplatforms for photodynamic therapy"</i> |
| 16:00-16:30 | Marco Milanese, UPO <i>"Preparation of new photoactive hybrid nanocomposites, based on hydrotalcite and saponite layered materials"</i> | 10:45 | Coffee-break |
| 16:30 | Coffee-break | 11:15-12:00 | Ruben D. Costa, FAU Erlangen <i>"Hybrid organic-inorganic materials for optoelectronic devices"</i> |
| 17:00 -17:45 | Frederic Labat, Paristech <i>"DFT modeling of sensitized solar cells"</i> | 12:00-12:30 | Federico Bella, POLITO <i>"Light-induced design of smart materials for energy devices"</i> |
| 17:45-18:10 | Carlo Nervi, UNITO <i>"Photoelectrochemical Cells for Solar Fuels: Water Splitting and CO₂ Reduction"</i> | 12:30-13:00 | Giuseppe Paternò, IIT/POLIMI <i>"Ultrafast Spectroscopy of Low-Dimensionality Organic and Hybrid Materials"</i> |
| 18:10-18:35 | Claudio Minero, UNITO <i>"The photocatalytic performance of Graphene-TiO₂ Hybrid materials"</i> | 13:00 | Closing remarks |
| 18:35-19:00 | Gianmario Martra, UNITO <i>"Radiative vs radiationless decays of photoexcited dyes entrapped in inorganic matrices: any possibility to manage the competition?"</i> | | |
| 19:00 | Poster session with buffet | | |

Abstracts

Oral contributions

O.1. Tailoring Optoelectronic Properties of Host-Guest Metal-Organic Frameworks (MOFs)

Abhijeet K. Chaudhari¹ and Jin-Chong Tan¹

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Metal-Organic Framework (MOF) is one of the most promising hybrid materials for future optoelectronics in light of its highly tunable physical and chemical properties [1]. Notably MOFs possess two active sites for tuning their optoelectronic characteristics, viz. metal corners and organic linkers. In principle by varying these two basic building blocks, the optical and electronic structures of the 3D periodic compounds can be manipulated [2]. The nanosized pores in MOFs offer long-range active coordination voids (“host” nanocage pore size < 10 Å) which could be utilised to confine and encapsulate functional “guest” chromophore molecules, manipulating energy transfer, and tuning energy and charge transport mechanisms of the resultant “guest@host” composite system. In this talk, I will discuss recent developments in this topic area, and illustrate two examples from my laboratory. The first exemplar employs an in-situ guest trapping strategy, we achieved nano-caging of a bulky emissive metal complex guest (ZnQ: Zn-bis-8-hydroxyquinoline) within the internal voids of the zeolitic imidazolate framework-8 (ZIF-8) host, resulting in a ZnQ@ZIF-8 system [3]. Another striking result concerns, the major improvement observed in the photophysical stability of the luminescent guest species upon nanoconfinement inside ZIF-8 pores. We established that, the nanoscale cavity of MOF could act as a protective vessel thus shielding light-sensitive fluorophores against rapid photochemical decomposition processes. The second example [4] concerns the use of a facile supramolecular approach to synthesise readily exfoliable MOF 2D nanosheets, functionalised in-situ adopting the guest@MOF strategy. We discovered that this new class of functionalised nanosheets has the potential to be used as smart sensors for accurate (reversible) recognition of a large number of volatile organic compounds (VOCs), and for next-generation lighting applications.

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O.2. Scale up of Zr-based “UiO-66” MOFs

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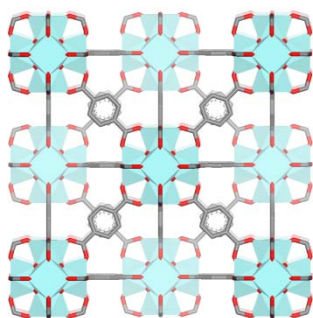
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Throughout the decade, Metal-organic frameworks (MOFs) have received considerable interest in both academic and industrial research[1]. MOFs are crystalline, porous, three-dimensional materials comprising metal ions or clusters coordinated to often organic molecules. The number of frameworks showing high chemical and thermal stability is increasing, leading MOFs forward as a viable solution for industrial processes.

A series of Zr-based MOFs developed and patented by University of Oslo, called UiO-66 (UiO=Universitet i Oslo) are among the most stable frameworks with its remarkable thermal and chemical stability[2]. Due to strong chemical resistance of UiO-66 frameworks these material are proposed as a promising candidates for adsorbed natural gas storage (ANG)[3], adsorption heat pumps (AHP)[4], Capture of toxic industrial chemicals (TIC)[5] and catalysis.

In general testing of MOFs and also of UiO series for industrial applications is wide spread over different technology readiness level (TRL2-5). However optimization of the synthesis, process and cost for industrial scale-up is seldom investigated. Most of the reported syntheses of UiO-66 are carried out in DMF, using corrosive solvents under high pressure and temperature condition which cannot be easily applied in industrial upscale.

In this presentation I will show the results of upscaling of UiO-66 with optimized reaction conditions that are adaptable in industrial production of MOFs.



UiO-66-BDC



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O.3. Preparation of new photoactive hybrid nanocomposites, based on hydrotalcite and saponite layered materials

Marco Milanesio,¹ Eleonora Conterosito,¹ Valentina Toson,¹ Davide Saccone,² Nadia Barbero² Luca Palin,¹ Claudia Barolo² Valentina Gianotti,¹ Enrico Boccaleri,¹ Iacopo Benesperi,^{2,3}

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New low cost photoactive hybrid materials based on organic luminescent molecules inserted into hydrotalcite (LDH) and saponite were produced, exploiting the high throughput liquid assisted grinding method (LAG) and hydrothermal methods [1-3]. These materials are conceived for application in dye-sensitized solar cells (DSCs) as co-absorber, or in silicon photovoltaic (PV) panels to improve their efficiency, being able to emit where PV modules show maximum efficiency. Organic molecules showing large Stokes' shift were designed, synthesized, and intercalated into LDH and saponite [4]. Two dyes already used in DSCs were also intercalated producing two new nanocomposites. Intercalation in inorganic matrices allows improving the stability of organic dyes and a direct use in polymer melt blending. The prepared nanocomposites absorb sunlight from UV to visible, emitting from blue to NIR, and thus are exploitable for light energy management. Finally, the best nanocomposites were dispersed by melt blending into a PMMA-PnBA block copolymer. In this way, photoactive films useful in the PV industry were obtained and characterized [4].

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O.4. DFT modeling of sensitized solar cells

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Third generation solar cells, which gather new solar cell concepts with very low cost and/or very high efficiency, are probably the most appealing solar cells today. They include multijunction solar cells, organic photovoltaic cells and also organic/inorganic or inorganic/inorganic hybrid devices, such as dye-, quantum dot- and perovskite-sensitized solar cells. They generally combine low-cost materials and fabrication techniques, [1] to the possibility to overcome the theoretical power conversion efficiency limit of 31% of single junction devices established by Shockley and Queisser [2]. They can take the form of transparent, thin and flexible sheets performing effectively in dim and diffuse light, and can be used indoors, as building-integrated power sources or in mobile electronic devices. These advantages largely offset their lower photoconversion efficiencies when compared to that of more conventional crystalline silicon cells.

In this contribution, we present application of a DFT-based computational protocol[3-5] to selected dye- and quantum-dot sensitized solar cells systems, with a particular emphasis on interfaces and experimental macroscopic data calculation.

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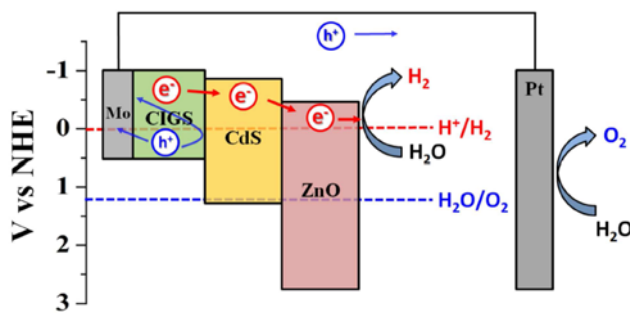
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O.5. Photoelectrochemical Cells for Solar Fuels: Water Splitting and CO₂ Reduction

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The need for a radical breakthrough in energy supply technologies can be ideally pursued by the so-called “Solar Fuel” approach.^{1a} However, artificial photosynthesis of organic molecules is still far away from providing real-world solutions. Practical considerations on the existing technology suggest that the most functional approach would be photovoltaic.^{1b} Nevertheless several hybrid approaches must be considered and deeply explored with the aim of finding a real breakthrough in the field of solar energy conversion. In this communication two kind of PEC (Photoelectrochemical Cells) for water splitting applications are presented: the first PEC is made by a film of Cu(InGa)Se₂ (CIGS) / CdS / ZnO / Pt (showing one the the highest reported photocurrent density of 32.5 mA/cm² under 1.5 AM illumination at a pH of 9),^{2a} and the second is made by cheap Cu₂O particles, supersonically sprayed onto an indium tin oxide (ITO) coated soda lime glass (SLG) substrate, without any solvent or binder. Annealing in air converted the Cu₂O films to CuO, with a corresponding decrease in the bandgap and increase in the fraction of the solar spectrum absorbed. The nanotextured p-type cupric oxide (CuO) films deposited via a low-cost scalable supersonic cold spray method in open air conditions,^{2b} produced a largescale CuO film. When used as hydrogen evolution photocathodes, these films produced photocurrent densities (PCD) of up to 3.1 mA/cm² under 1.5 AM illumination.



The conversion of CO₂ into valuable chemicals/fuels is a perfect way for approaching the contemporary challenges of green-house emission and depletion of fossil energy resources. However, PECs for CO₂ reduction are in their infancy, and a suitable catalyst has still to be found. The quest of an efficient catalyst for CO₂ reduction can be pursued using electrochemical techniques. In this presentation a brief overview of recent advances in the use of organometallic complexes as catalysts for electrochemical CO₂ reduction will be illustrated, in particular the properties of Re(bpy) and Mn(bpy) complexes.³

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O.6. Radiative vs radiationless decays of photoexcited dyes entrapped in inorganic matrices: any possibility to manage the competition?

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Internal conversion is the main competitor of the technological exploitation of electronic excited states of organic molecules for producing light or inject energy in materials and/or molecules. The hybridization with inorganic matrices can pave the way toward a proper management of the competition, provided the disclosure of key aspects of the preparation methods and/or of the organisation of guest molecules within the inorganic host ruling effective functional performances. In this respect, elements for a rational engineering of hybrid nanoparticles resulting from the entrapment of indocarbocyanine dyes in nascent silica nanospheres highly homogeneous in size and shape [1,2] and for the understanding of structural and photophysical properties of dyes confined in zeolite channels up to the formation of nanoladders [3,4] will be presented and discussed.

Acknowledgments

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- CRT Foundation, Reserach&Education First Call 2014 “A regional network connecting nano- and neuroscience: toward the rational design of nanoparticles as tools for neurobiology” (<http://life-9.weebly.com>)
- FIRB Call 2012, project RBFR12CLQD: “Impose Pressure and Change Technology – IMPACT” (www.impact-firb.it)

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O.7. The photocatalytic performance of Graphene-TiO₂ Hybrid materials

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The two classes of hybrid materials (a) semiconductor-on-graphene and (b) graphene-on-semiconductor are presented. For class (a) the graphene nanoparticles (GNP) can be strictly controlled. The semiconductor is synthesized in situ. GNP functionalization induces the nucleation of TiO₂ NPs with specific shapes and crystalline facets exposed. COOH functionalization directed the synthesis of anatase truncated bipyramids, bonded to graphene sheets via the {101} facets, while NH₂ functionalization induced the formation of belted truncated bipyramids, bonded to graphene via the {100} facets. [1] GNP(COOH)-TiO₂ composites were more efficient at abating phenol than those synthesized on NH₂-functionalized GNP. However, neither of these composites was stable under irradiation. The addition of oleic acid or ethylenediamine (EDA) stabilized the materials under irradiation; however, only GNP(COOH)-TiO₂-EDA showed a significant increase in phenol degradation rate, better than that obtained with TiO₂ alone. This result can be attributed to Ti-OH complexation by EDA, which protects GNP from oxidation. It was supposed that the orientation of the most reducing {101} facets toward GNP and the most oxidizing {100} facets toward the solution induces faster phenol degradation owing to a better separation of the charge carriers. [1]

For class (b), graphene is typically synthesized on preexisting semiconductor particles by reduction of graphene oxide (GO to rGO). The stability of such materials can be poor.[1] Experiments using hybrid materials synthesized at different loadings of rGO by chemical reduction with hydrazine in the presence of nanometric TiO₂ and SiO₂, are here compared with naked oxides using phenol and methylene blue (MB) under two different irradiation conditions (UV-Vis and Vis only light). The analysis of the photocatalytic behavior of the materials underlined its complexity as the working mechanisms depend not only on the degraded substrate, but also on the kind of irradiation adopted. A careful optical characterization of the hybrid materials and lamp emission spectrum allows disentangling many tricky rate trends observed changing % rGO in the hybrid catalyst.

Phenol does not absorb in near UV and is degraded predominantly via UV-based photocatalytic mechanism and rGO decreases the rate by increasing the amount of scattered light. MB is degraded via UV-based photocatalytic mechanism and in the case of Vis irradiation via a dye-sensitized mechanism. Vis-sensitization driven by rGO phase seems not to be the predominant mechanism in the studied experimental conditions and with the studied photocatalytic materials. However, rGO plays a key role for adsorption and as electron passageway for dye-sensitized mechanism. Because the adsorption of MB on the TiO₂ surfaces activates dye-sensitized processes which are not directly related to the real photocatalytic features of the hybrid materials, studies that use MB alone with hybrid materials and illumination with not well characterized emission spectrum, could lead to misleading conclusions on the role of rGO.

When TiO₂-rGO composites are synthesized through a hydrothermal method using graphene oxide and commercial P25 as starting materials (at two different ratios 1:10 and 1:5), the photocatalytic efficiency of the composite materials for risperidone (antipsychotic drug) removal in distilled water, as well as in different surface waters at natural pH, under simulated solar light and almost Vis light irradiation was always larger than that of bare TiO₂-P25, irrespectively of the aqueous matrix composition. [2] The risperidone molecule does not absorb in near-UV e Vis wavelengths.

Among many mechanisms reported on the role of rGO, the above results strongly suggest that the working mechanism involves electron transfer from rGO onto the titania, and eventually holes migration from titania to rGO, where adsorbed substrates are oxidized. This last oxidation is possible only if the HOMO has higher energy (less positive standard redox potential) than the empty states of excited rGO, supposedly for MB and risperidone, and not for phenol. Then, reduced graphene is advantageous when substrates are adsorbed and when the charge separation is possible (coupled with a proper semiconductor like TiO₂). Alone, or coupled with low working function oxides like SiO₂, rGO is ineffective.

It is not possible to fully generalize the conclusions obtained on the photocatalytic behavior of the materials we synthesized to the entire set of reported TiO₂-rGO materials, because the both the TiO₂ phase contact and the degree of rGO reduction can influence the energy position of rGO LUMO allowing/hindering the electron injection from/toward adsorbed species, and can affect abruptly the photocatalytic performance.

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O.8. Metal Organic Frameworks as potential photocatalysts. Where are we and where are we heading?

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Metal-organic frameworks (MOFs) have attracted a great deal of interest during the last decades due to their unprecedented surface area, remarkable tuneability and the fascinating variety of possible combinations of constituting blocks. Several applications have been suggested, such as separation of gases,^{1,2} catalysis,³ drug delivery and sensing.⁴ Photocatalysis was proposed in the early 2000s inspired by an intuitive analogy between them and their corresponding oxides, often being semiconductors.^{5, 6} Despite the fact that the early reports of semiconducting properties of MOFs have been disputed,^{7, 8} this initial misconception led to the application of frameworks based on Zn, Ti and other transition metals in a variety of photocatalytic reactions such as oxidation of organic compounds,^{9, 10} reduction of metal ions¹¹ and synthesis of solar fuels.¹² In this lecture, we will give an overview of these applications and our recent efforts in understanding how photocatalysis works on different MOFs along with certain rules for design of superior MOF based photocatalysts.^{13, 14, 15}

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O.9. Drawing from natural materials for organic electronics

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Materials of biological origin are extremely attractive for integration in organic electronics, since they open access to relevant applications as bio-compatible and sustainable devices. Bringing together components from biology and from synthesis requires innovative and interdisciplinary approaches, for which it is necessary to merge different competences. In particular, the possibility to draw fully from natural raw materials for developing new generation electronic devices represents a frontier of great technological impact. In this communication, different strategies for the combination of the functions of organic semiconductors with the additional features of biological molecules are presented.

The decoration of conjugated polymers and oligomers with small biomolecules, like L-phenylalanine and D-glucose, enables access to organic semiconductors that show interesting interaction with chiral environment and circular polarized light.¹

The bioconjugation of a photoenzyme, the Reaction Center (RC) from the bacterium *Rh. Sphaeroides*,² to synthetic fluorophores, producing enzymatically active bio-hybrids, is described. The fluorophores can be covalently linked to the photoenzyme, extending its efficiency in the visible spectrum.³ The same chemistry is used to anchor photoenzymes onto evaporated organic pigments thin films that display protein induced photosensitization.⁴

Finally, the preparation and manipulation of novel cellulose nanofibers freestanding thin films, known as "nanopaper" is described. Nanopaper represents an environmentally harmless substrate and component for organic devices. Functionalization chemistry on the nanofibers, both in solution and in heterogeneous conditions, can be used to modulate surfacial properties of nanopaper and its environmental stability. Hydrophobization dramatically improves the water resistance yielding ideal substrates for electronic devices.⁵

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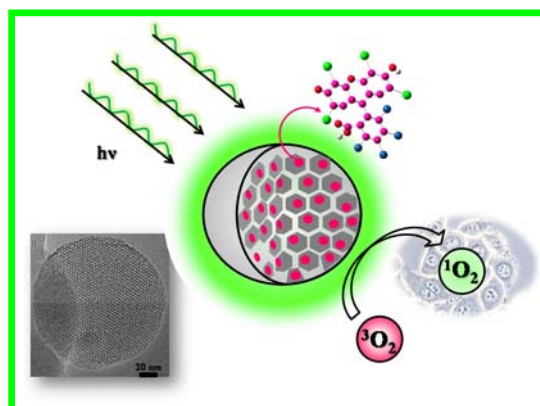
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O.10. The therapeutic effect of light: hybrid nanoplatforms for photodynamic therapy

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Photodynamic therapy (PDT) is an emerging treatment for a variety of oncological diseases¹. PDT is based on the concept that photosensitizer molecules (PS) generate singlet oxygen ($^1\text{O}_2$) upon irradiation, which acts as the primary cytotoxic agent responsible for irreversible damage of the treated tissues. This treatment offers the advantage of an effective and selective method of destroying diseased tissues without damaging adjacent healthy ones. To increase the cell uptake and to protect the PS from photochemical degradation, it is necessary to incorporate covalently the PS within biocompatible delivery vehicles. Among the various vehicles, mesoporous silica nanoparticles (MSNs) have attracted great interest due to their topology that provides three distinct domains that can be independently functionalized: the silica framework, the hexagonal pores, and the nanoparticle's outermost surface, thus incorporating the essential capabilities of a theranostic platform in a single particle. In addition, MSNs have demonstrated high in vivo biocompatibility, straightforward surface functionalization and avid cell uptake². In this contribution, we report a simple surface modification process that conjugates a PS, Rose Bengal (RB)³ or Visudyne®⁴, with amino-functionalized MSNs through covalent bonding. Several hybrid systems with different PS loading were prepared to optimize the PS concentration and to obtain a high efficiency of $^1\text{O}_2$ release. RB-modified MSNs have shown a relevant photostability and a high efficiency in the singlet oxygen generation³. In vitro tests have evidenced that these photoactive systems are able to reduce cell proliferation in one of the most aggressive skin cancer types after light irradiation. The RB-MSNs hybrid materials represent the first step in the design of multifunctional nanoplatforms for cancer theranostics (imaging, targeting and therapy).



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O.11. Hybrid organic-inorganic materials for optoelectronic devices

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Hybrid organic-inorganic optoelectronics are heralded as the next generation of lighting and photovoltaic technologies.¹ In this context, our efforts encompass three main actions, namely the development of suitable third generation of electroluminescent materials for ionic-based lighting devices, the application of nanocarbon-based hybrids in solar cells and lighting devices, and the development of bio-inspired components for lighting, energy conversion, and diagnostic applications.

Herein, the implementation of the third generation of materials – *i.e.*, lighting perovskite nanoparticles, small molecules, and copper(I) complexes – for light-emitting electrochemical cells (LECs) will be presented as new approaches to develop deep-red, blue, and white lighting sources.² Next, carbon nanohorns will be shown as new integrative components for preparing new nanocarbon-hybrid dye-sensitized solar cells (DSSCs), resulting in several breakthroughs, namely i) the enhancement of charge transport and collection in the electrodes, ii) the development of iodine-free, solid-state electrolytes, and iii) the fabrication of platinum-free counter electrodes.³ Finally, a new strategy to stabilize any type of bio-components – *i.e.*, enzymes, fluorescent proteins, *etc.* - in a rubber-like material was developed. As an example, the latter was applied to fabricate the first bio-inspired hybrid light-emitting diodes featuring a bottom-up energy transfer protein-based cascade coatings. The synergy between the excellent features of fluorescent proteins and the easily processed rubber produces bio-HLEDs with less than 10% loss in luminous efficiency over 100 hours.⁴ Currently, other applications like bio-reactors and ready-to-go-kits are under development in our laboratory.⁴

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O.12. Light-induced design of smart materials for energy devices

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The stability of energy devices is a critical (but often disregarded) issue, since great focus is often devoted to the efficiency records (even if these values rapidly decrease upon time). However, today's research in the energy field must be connected to concepts such as long-term stability, safety and environmental impact.

In this work, we present free-radical photopolymerization as an attractive technique for the design and straightforward preparation of polymeric components for different energy devices (both storage and conversion). Photopolymerization represents a very attractive technique to this purpose, since it does not require solvents, catalysts, thermal treatments and purification steps.

The design of multifunctional photopolymers for dye-sensitized solar cells [1], perovskite solar cells [2], lithium-ion batteries [3], sodium-ion batteries [4] and photoelectrochromic devices [5] is demonstrated as an effective way to improve the stability (and sometimes also the efficiency) of these highly-in-vogue energy conversion and storage devices.

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O.13. Ultrafast Spectroscopy of Low-dimensionality Organic and Hybrid Materials

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Ultrafast spectroscopy is a very useful tool to investigate the photophysical features of functional materials, as organic molecules, polymers, carbon related low-dimensional structures and inorganic nanosystems.

In this work we describe the basic working principles of pump probe technique and we report few examples about the temporal and spectral behaviour of the photo-generated species in the aforementioned materials. These include, in particular, graphene quantum dots [1,2], squaraine derivatives [3], and polymer/nanocrystal heterojunctions [4] of high interest for light emission and photovoltaics.

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Abstracts

Poster contributions

P. 1. Unravelling design guidelines for photocatalytic metal-organic frameworks

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New materials capable to provide non-fossil fuels are key to ensuring sustainable global energy supplies. Sunlight is by far the largest exploitable resource, thus mimicking natural photosynthesis has been an attractive strategy to achieve solar-to-chemical energy conversion. However, systems able to efficiently harvest and store this energy are still lacking.

Metal-organic frameworks (MOFs) are highly tuneable 3D-nanoporous structures composed by organic linkers and metal nodes. MOFs have been used recently as custom designed materials for artificial photosynthesis, i.e. showing to be able to reduce CO₂, and evolve H₂, yet their performance is limited.¹ Fundamental understanding of photocatalysis by MOFs has the potential to move forward this field greatly.

MOFs containing d⁰ metals such as NH₂-MIL-125(Ti) and NH₂-UiO-66(Zr/Hf) are among the most studied for photocatalysis. We found that the photocatalytic proton reduction by NH₂-MIL-125(Ti) is much more efficient than by the Zr/Hf UiOs, despite their structural similarities. As revealed by quantum chemistry, EPR measurements and transient absorption spectroscopy (TAS), only in the case of the Ti-based MOF the highest occupied and lowest unoccupied orbitals promote a long lived ligand-to-metal charge transfer (LMCT) upon photoexcitation, making this material suitable for photocatalytic applications.²

Furthermore, MOFs are well known for their versatility via functionalization of their organic counterpart. In this context, we compared MIL-125(Ti) structures containing different linkers. We demonstrated via ultrafast spectroscopy that the choice of the linker has a profound effect in the lifetime of the photoexcited state and that the efficient charge separation hinders recombination and hence improves the photocatalytic rate, allowing chemical reactions to take place.³

These results highlight the importance of the excited state kinetics when selecting MOFs for photocatalysis, being ligand functionalization the key for rational design.

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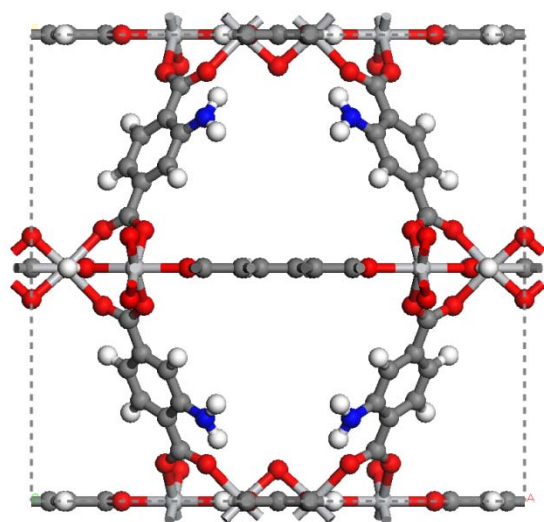
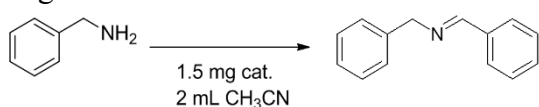
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P. 2. Benzylamine coupling catalysed by MIL-125-NH₂

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Aerobic oxidation of benzylamine to N-benzylidenebenzylamine is an important reaction in organic chemistry since the product is a valuable intermediate in organic synthesis.¹ Being the reaction conducted in presence organic peroxides, the possibility to use molecular oxygen as oxidizing agent is foreseen although it is often accompanied by the formation of several byproducts.¹ The individuation of new catalysts for this reaction is then a hot topic of research. Metal organic frameworks (MOFs) are hybrid organic –inorganic materials that have shown exceptional performances in several fields of applications. N-hydroxyphthalimide modified iron based MOFs employed as catalyst in oxidation of benzylamine have shown conversion as high as 96% at 100°C after 24 h.² MIL-125 and its amino-analogous MIL-125-NH₂ are titanium



oxide-based MOFs successfully applied as photocatalysts in several oxidative reactions.³⁻⁶

In this study, the ability to exploit MOFs as photocatalysts for this reaction at RT was explored for the first time. MIL-125-NH₂ was synthesized by following a recipe reported in the literature and it was fully characterized by means of X-ray diffraction, nitrogen volumetry, infrared and UV-vis spectroscopies. Its activity as photocatalyst for benzylamine condensation was tested irradiating the batch with a Xe lamp for 6 h. A yield of 78% was obtained in presence of the MIL-125-NH₂, whereas in absence of a catalysts it dropped to only 40%. The use of two different filters, for $\lambda > 385$ nm and $\lambda > 450$ nm, allowed to verify that whereas for $\lambda > 385$ nm the activity was maintained unaltered, with the $\lambda > 450$ nm filter it

dropped to the same value obtained in dark at 60°C.

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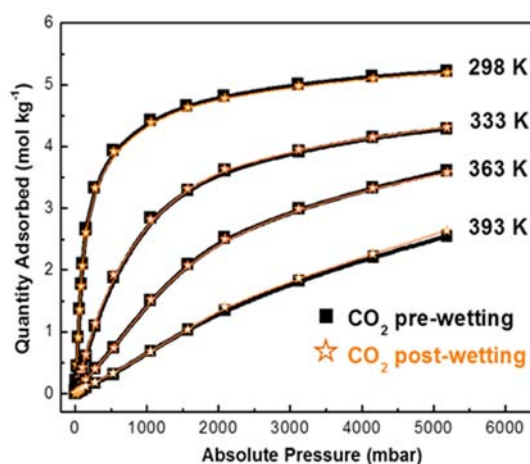
P.3. Reversible water adsorption at room temperature in an amine-free MOF for CO₂ separation: towards real post-combustion capture

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Metal-organic frameworks (MOFs) with permanent porosity are one of the most promising and efficient materials for Carbon Capture Utilization and Storage (CCUS). Their strength consists in a high volumetric capacity of CO₂, selectively captured with respect to other gaseous competitors (N₂ or O₂).^{1,2} However, MOFs are often sensitive to water, representing the 5-20% of coal and natural gas-fired power plant exhaust.³ This work intends to prove the high technological relevance of UTSA-16 MOF⁴ for post-combustion CCS highlighting, among the other properties, the ability of reversibly adsorbing CO₂ in the presence of water vapour, like no other amine-free MOF.⁵ This cutting-edge aspect was evaluated by a combination of different experiments such as CO₂-H₂O gravimetric adsorptions and CO₂ breakthrough analysis (up to 160 cycles) in dry and wet conditions. Moreover, the strong IAST selectivity of UTSA-16 for CO₂ was calculated with respect to N₂ and O₂ from volumetric isotherms performed at 1 bar and different relevant temperatures (298, 333 and 363 K). Beside a medium strength isosteric heat of CO₂ adsorption (38 kJ mol⁻¹),⁶ UTSA-16 showed a N₂ isosteric heat which is 10 kJ mol⁻¹ lower than what calculated for Mg₂(dobdc), one of the most representative MOFs for CO₂ capture.⁷ Dynamic experiments on CO₂ (breakthrough), N₂ and O₂ (pulsed chromatography) confirmed the static experiments results, indicating UTSA-16 as a stable and efficient MOF for real post-combustion processes.



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P.4. Synthesis and characterization of a Ce-based metal-organic framework (MOF)

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MOFs⁽¹⁾ are porous crystalline materials built from organic linkers and inorganic metal (or metal-containing clusters) nodes. These materials can be exploited in many industrial processes like heterogeneous catalysis, gas adsorption and capture, i.e. CO₂ sequestration.

In this work a synthesis of a very recently prepared⁽²⁾ Ce-based MOF made from terephthalic acid ligand (H₂BDC) and Ce cations is reported both by classical solvothermal and microwave-assisted methods together with a preliminary characterization (by means of PXRD, TGA, SEM, FTIR, Raman, XAS), followed by a surface area (by means of N₂ adsorption), active sites (by means of in-situ FTIR CO adsorption) and a volumetric and calorimetric CO₂ adsorption characterization. Finally also optical absorption and emission properties are measured (DR-UV-Vis and emission spectra).

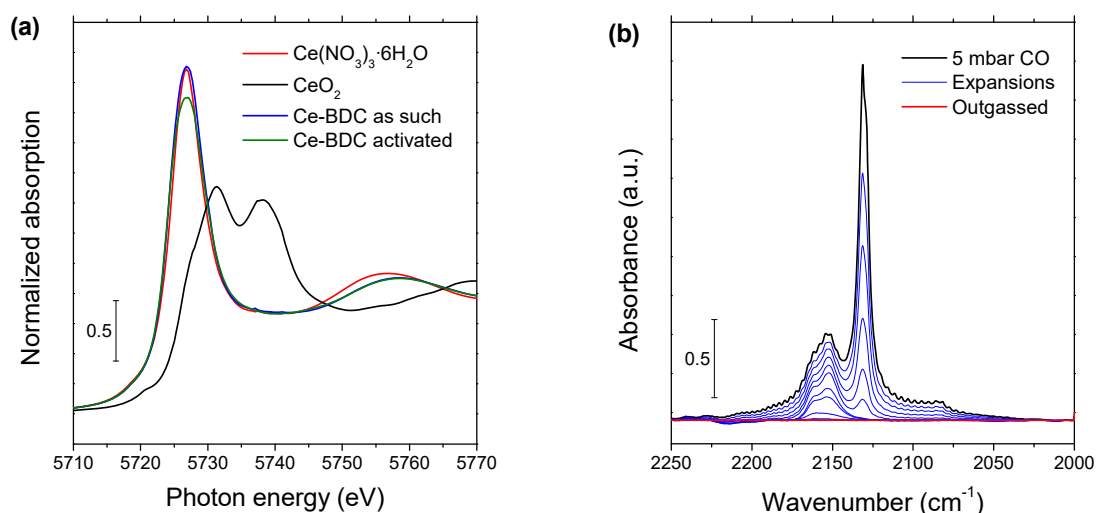


Figure 1 – a) XANES spectrum of CeBDC with Ce³⁺ and Ce⁴⁺ standards. b) Background subtracted FTIR spectra of adsorbed CO at 77K on CeBDC activated at 350°C in vacuo.

The solvothermal synthesis optimized procedure gives rise to a MOF with high purity and acceptable yield (about 85%). The microwave variant is capable to do it even faster. The crystal structure is very complex, with five Ce atoms different by symmetry in the unit cell, and shows 2D channels filled with DMF. Upon thermal treatment, these molecules are lost (above 250°C in vacuo) with a rearrangement of the crystal structure and an increase of the accessible surface area. This value, as high as 300 m²/g, is quite low for a MOF⁽¹⁾ and explains the low CO₂ uptakes observed.

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P.5. A series of new metal-organic frameworks based on Ce cations and dicarboxylic acids

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Porous metal-organic frameworks¹, thanks to the infinite variety of combining cationic nodes and linkers, generate an unlimited number of structures, characterized by specific porosity and functions that open large possibilities in many areas of technological relevance, like heterogeneous catalysis or gas sorption.

In a previous work² a detailed characterization of a Ce terephthalate MOF showed a low surface area and, for this reason, poor sorption performances. In order to improve this feature a series of Ce MOFs with longer linkers (figure 1) has been synthesized with the aid of solvothermal high-throughput³ methods using DMF as solvent and cerium nitrate as metal source.

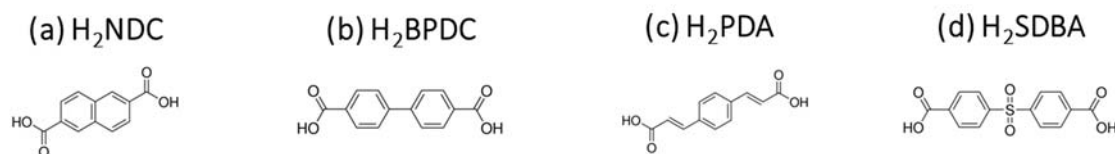


Figure 1 – Skeletal formulas of the used linkers: a) 2,6-Naphthalenedicarboxylic acid b) Biphenyl-4,4'-dicarboxylic acid c) 1,4-Phenylenediacyrylic acid d) 4,4'-Sulfonyldibenzoic acid

The synthesis conditions of the resulting products (which will be called respectively CeNDC, CeBPDC, CePDA and CeSDBA) were optimized. The crystal structures of the first two MOFs were also determined by single crystal diffraction. The full characterization of these compounds by means of physical-chemical techniques (TGA, *in-situ* FTIR, N₂ volumetry) is still a work in progress. Preliminary TGA data showed that CeNDC can be desolvated without a structure collapse.

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P.6. NIR-Absorbing polymethyne dyes as DSCs sensitizers

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Since their publication in 1991 by O'Regan and Grätzel, dye-sensitized solar cells (DSCs) have undergone an intensive research, with power conversion efficiencies constantly growing up to 13% (1). One of the main ways to improve the efficiency of a DSC is to extend the light-harvesting region into the near-infrared (NIR) region of the spectrum (2), a feature which is commonly achieved by modifying the sensitizer's structure. Among metal-free sensitizers, polymethyne dyes as squaraines, croconines and cyanines are known for their sharp NIR absorption bands with high molar extinction coefficients, combined with easily tunable synthetic procedures and considerable photostability (3).

We present here the synthesis, spectroscopic and photovoltaic characterization of a series of squaraines, cyanines and croconines which were thoroughly engineered in order to extend their absorption in the NIR region of the spectrum. Absorption maxima were shifted up to 830 nm, with molar extinction coefficients as high as $320000 \text{ mol}^{-1} \text{ cm}^{-1}$.

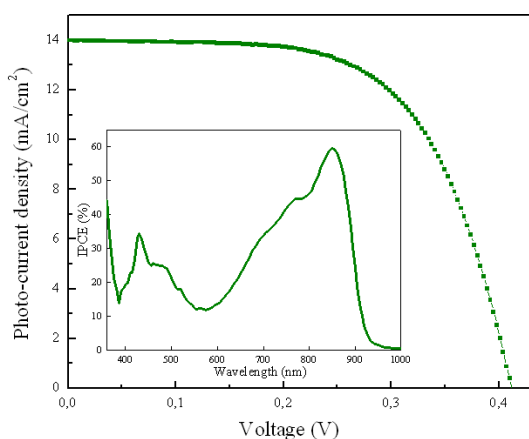


Figure 1. Photocurrent density–voltage and IPCE curves of cyanine VG20.

These characteristics allowed to reach up to 60% IPCE at 850 nm, with a record conversion efficiency of 3.6%, by means of carefully optimized cell parameters.

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P.7. Gold Nanoparticles usable for photothermal therapy: a study of the interaction with Mucin

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Gold Nanoparticles (GNPs) are highly attractive constructs for tumor therapy due to their ease of synthesis, tunable near-infrared (NIR) localized surface plasmon resonance (LSPR), and large, functionalizable surface areas (1). The LSPR enhances optical properties, giving rise to high absorbance, scattering, and two-photon luminescence phenomena that can be exploited for **photothermal** or **photodynamic** cancer therapy and diagnostic imaging (2). Among issues modulating drug/nanomaterials absorption for every type of therapy, **mucus penetration** cannot be ignored. In fact mucus is the first **barrier** that xenobiotics must overcome to be absorbed and gain access to the circulatory system. The major constituents of mucus are water (95-99.5%) and high molecular weight **glycoproteins called mucins**. In the mucus these large oligomeric glycoproteins form networks which are a chemical and physical barrier that not only protect the epithelial but also limits the use of oral administered and inhalatory drugs or nanomaterials. Both secreted and membrane-bound mucins are well established as tumor markers, as they are commonly **overexpressed**, underglycosylated and associated with a poor prognosis in many **carcinomas**. Two main mechanisms limit diffusion through mucus gel: a) interaction with mucus components (i.e. electrostatic and hydrophobic interactions with mucins) and b) size filtering related to the size of the mesh spacing between the mucin fibers. In the design of a putative drug delivery nanoparticle, one may expect the nanoparticles to be able to traverse the mucus barrier if its size is smaller than the mesh size of the network (10–250 nm), and should not experience strong hydrophobic, electrostatic or hydrogen bond interactions with the mucin. Further, the nanoparticles will need to penetrate the mucus faster than its characteristic clearance rate. Conventional nanoparticles commonly fail in one or more of these points and thus, to overcome this problem, to achieve longer residence times for drugs at absorption sites, there is a need to design mucus penetrating nanoparticles (3). This study highlights the interaction between mucin glycoprotein, mucin from porcine stomach Type III (PGM), and GNPs and functionalized GNPs under physiological conditions, in order to investigate the affinity of the nanoparticles to mucin. This aspect could be of the utmost importance for the use of GNPs for biomedical purposes as photothermal therapy.

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P.8. Resorbable hollow fibers for the delivery of photosensitive drugs

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Recent developments in biophotonics have raised growing interest towards the formulation of new materials with an optimal combination of optical properties and biocompatibility [1]. Noticeable research effort is spent in the development of minimally invasive techniques devoted to deliver opportune light sources and light-activated substances to selected tissues, without affecting surrounding organs. However, there is still a lack of experience in combining in one device the delivery of light with the opportune local administration of photosensitive drugs. In the present work we propose the use of resorbable phosphate glasses as new materials for combined light and drug delivery, featuring transparency from near UV to near IR region, solubility in simulated physiological conditions and thermal stability for fiber drawing [2]. We explore the employment of specialty hollow glass fibers for the controlled release of drugs, in order to limit the side effects of systemic drug administration. Preliminary results show that surface interaction between glass and molecules plays a key role in the release of drugs.

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P.9. Study and optimization of light-emitting electrochemical cells based on heteroleptic [Cu(N[^]N)(P[^]P)]⁺ complexes

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In the last years, Cu(I) complexes have been identified as favourable candidates as active materials in light-emitting electrochemical cells (LECs). They represent in fact a cheap alternative to Ir (III) complexes. In particular, heteroleptic copper(I) complexes belonging to the [Cu(N[^]N)(P[^]P)]⁺ family exhibited encouraging results^[1]. Therefore, we decided to synthesize, characterize, and compare in LECs two Cu(I) complexes, namely [Cu(2,2'-bipyridine)(POP)]PF₆ (**1a**) and Cu(2,2'-bipyridine)(6,6'-dimethoxy)(POP)]PF₆ (**1b**)^[2].

We effectively proved that the device performances of **1b** are better than those of **1a**. In particular, we obtained a 3 times higher efficiency together with an extended lifetime under pulsed current. A further improvement in the stability of the device was obtained by using the organic 4,4'-Bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) to perform a host-guest system; a 10 times higher lifetime was in fact observed for both complexes along with a lower driving voltage, while the luminance remained comparable.

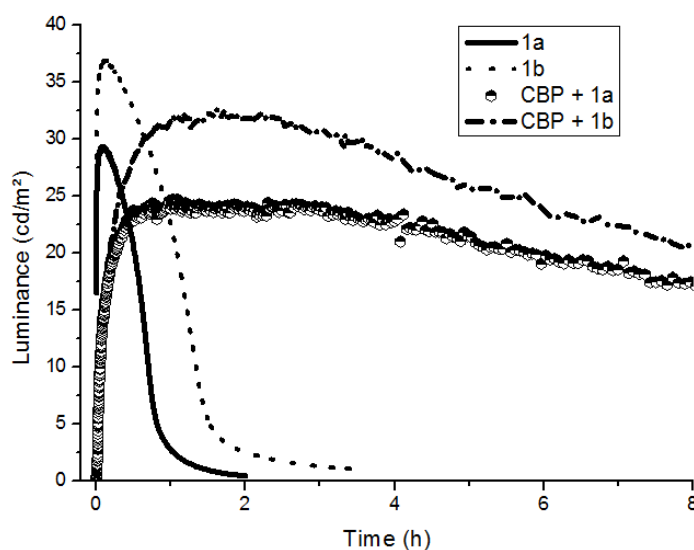


Figure 1. Luminance vs time graph for the various devices under PC (7.5 mA)

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P. 10. Study on gelled aqueous electrolytes for DSSCs with different redox mediators

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Dye sensitized solar cells (DSSCs) are a photovoltaic technology able to convert solar light into electricity and have recently achieved conversion efficiencies up to 14%. Nevertheless, DSSCs are not yet commercialized on large scale due to two particular aspects that have been poorly addressed, especially when it is considered that DSSC technology was conceived to be eco-friendly and inspired by photosynthesis. First, the standard electrolyte system is based on volatile organic solvents (*e.g.*, acetonitrile, methoxypropionitrile), also flammable and toxic, which certainly affect the safety requirements when the device is installed. Secondly, the polymer electrolytes that have been introduced as solid or quasi-solid matrices to increase the stability of DSSCs are typically macromolecules derived from the petrochemical industry, which makes the DSSC technology not so much sustainable as it was in the initial intent.

Above all, DSSCs with 100% water-based electrolytes appear as the best solution to reduce costs, increase safety, stability, and environmental compatibility, and have recently achieved efficiency up to 6% [1]. Moreover, the idea of gelling the aqueous electrolyte into a low-cost bio-derived polymeric matrix open the possibility to increase long-term stability, preserving DSSCs sustainability [2].

In this contribution, the study on fully aqueous electrolytes gelled with xanthan gum is presented. Thanks to our knowledge [3,4] and to a multifactorial approach (Design of Experiment, DoE), the effects on DSSCs performances in function of type (I/I₃⁺ vs Co-complex) and concentrations of the redox mediator are evaluated.

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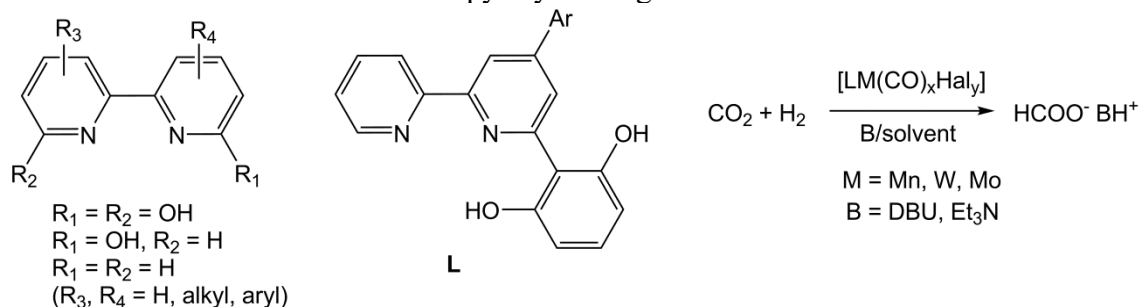
P.11. CO₂ hydrogenation catalyzed by Earth abundant transition metal complexes

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Design of ligands to enable metal-ligand cooperation in small molecule activation and hydrogenation/dehydrogenation reactions has been shown to play a significant role in many catalytic transformations.¹ Commonly, the presence of a “proton-shuttle group” is accepted as a justification that promotes activation of H₂ and CO₂, since it is able to give reversible protonation/deprotonation that is often accompanied by tautomerization¹. For instance, the Iridium complexes with bipyridyl and bipyrimidyl ligands containing two ortho-OH groups are effective catalysts for CO₂ conversion to formate as well as the reverse reaction, formate dehydrogenation². Mn complexes with functionalized bipyridyl ligands **L** were shown to catalyze electrocatalytic CO₂ reduction to formic acid and CO, with selectivity and efficiency different from their unsubstituted bipyridyl analogs.³



In this work we will report the results of a first screening of different complexes with pyridine-based ligands and “proton shuttle” groups based on first row transition metal (Mn, Mo, W).

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P. 12. ZnO tetrapod for UV sensors and dye-sensitized solar cells

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Zinc oxide tetrapod (ZnO-T) is the structure, consisting of 4 nanowires, is especially interesting for its simple synthesis and broad application possibilities, however growth mechanism is not thoroughly understood.

Here, we propose a simple non-catalytic one-step process method for an efficient and rapid synthesis of ZnO tetrapods by Zn vapor oxidation under air environment and application for fast UV sensors and dye sensitized solar cells (DSC).

ZnO tetrapod structure is possible to growth in ambient air conditions from Zn powder. Such anisotropic structures were obtained because of high Zn vapor pressure, favoring small nucleus diameter and fast kinetic growth. Gas phase growth gives advantages, as no purification is needed, ZnO-T powder can be collected downstream of the reactor. For application ZnO-Ts can be deposited directly on the needed surface or dispersed in solvents (water, ethanol, etc.) and a porous films of tailored thickness can be obtained.

ZnO-Ts provide direct pathways for electron transport, reduce recombination reaction, therefore are interesting for application in DSCs. It is expected that ZnO tetrapod film as photoelectrode of nanostructured ordered network with tailored porosity can advance the DSSC performance.

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P. 13. Aqueous Solar Cells: New Perspective in Photoelectrochemical Devices

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Dye sensitized solar cells (DSSCs) with high performances have been fabricated mainly with organic solvent-based liquid electrolytes. However, these solvents not only have high vapor pressure, but they are often toxic and flammable. In the last few years, the idea of moving towards a water-based or completely aqueous system clearly emerged [1].

DSSCs fabricated with aqueous electrolytes may offer reduced costs, non-flammability and environmental compatibility, but the presence of water in the cell may reduce the long-term stability as well as the photovoltaic performance. For this reason, in recent years, an increasing number of research articles has been published in this direction and new dyes, electrodes and electrolyte components are continuously proposed [2].

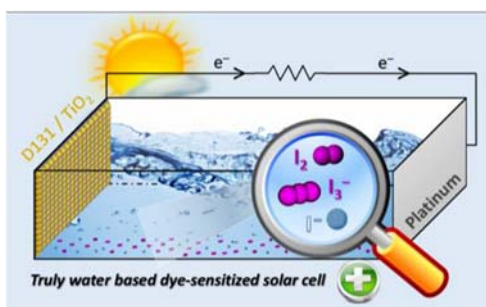


Fig. 1 Aqueous electrolytes for dye-sensitized solar cells.

In this work, the study of different dyes as well as truly aqueous electrolytes (Fig. 1) is presented. A few curious and anomalous behaviors observed in the literature and in our laboratories are investigated for this class of electrolytes [3]. Moreover, the development of a series of novel aqueous gel electrolytes based on natural polymers is also discussed as well as their interesting photovoltaic characteristics.

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P.14. New fluorescent systems with large Stoke shift based on multiple imidazo[1,5-a]pyridine

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A facile multiple condensation procedure, provides a versatile one step approach for the synthesis of multidentate nitrogen heterocyclic ligands containing the imidazo[1,5-a]pyridine moiety. These compounds show considerable optical properties, with good fluorescent emissions, moderate quantum yields and large Stokes' shifts enabling their technological application.

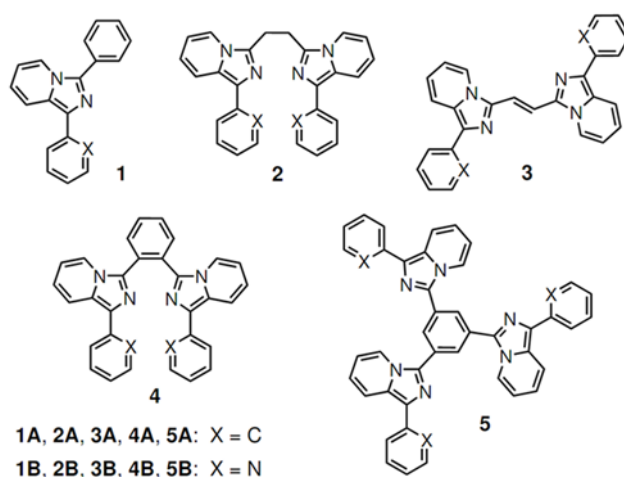


Figure 1. eneral structures of synthesized compounds.

The photofunctional diversity of the synthesized compounds imply that the bis/tris(1-(pyridin-2-yl)imidazo[1,5-a]pyridin-3-yl)benzene and their derivatives can potentially be used as easily tuneable photofunctional materials (organic host in hybrid structures)² and as tetradentate ligands of interest in the fields of DSCs, OLED, NLO and for pharmaceuticals applications.³ Moreover, high yields, absence of catalysts, high accessibility and stability, ease of handling and preparation, no toxicity derivatives render this synthetic approach particularly useful for a systematic screening and full-scale production and make the products inexpensive and affordable.

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P. 15. Chromophoric Linkers For Hybrid Materials

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In the last decades material chemistry played a central role in developing new structures both for energy related problems and biomedical application. In particular a number of hybrid organo-inorganic nanostructured systems has been explored for light harvesting and bioimaging.^{1,2} Most of these studies use the inorganic structure as an inert scaffold able to host photoactive molecules.³ In this work we report our first synthetic efforts in developing novel hybrid structures where the sensitizer is part of the scaffold. In particular we focussed on the synthesis of novel hybrid materials based on Zr-based nodes and squaraine dyes bearing two carboxylic units as linkers. Their peculiar properties will be investigated both in photovoltaics and photo dynamic therapy, where these chromophores already demonstrated an interesting activity.^{4,5}

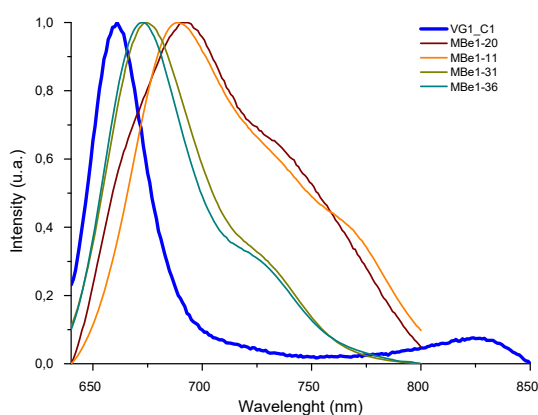


Figure 1. Absorption spectra of VG1_C1 and the related Zr-based hybrid materials

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P.16. Intercalation of photoactive neutral molecules into saponite layered materials

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Recently, the interest in the synthesis of organo-clays materials has increased, because the co-presence of different functionalities in the same material can be exploited for several applications such as catalysis, drug delivery, optoelectronics, and nanocomposites. The aim of the study was synthesizing low cost, stable and efficient light harvester hybrid organo-saponites. As a layered inorganic matrix was selected the saponite, a trioctahedral 2:1 clay mineral ($M^{n+}_{x/n}[Mg]_6(OH)_4[Si_{18-x}Al_x]O_{20} \cdot mH_2O$). According to the literature, two different treatments were considered and modified for the incorporation of neutral molecules. The one-pot synthesis¹, developed for the direct organomodification of saponite, allows obtaining directly in one step the incorporation of the neutral molecule. Conversely, the Liquid Assisted Grinding (LAG)², developed for the intercalation of anions into hydrotalcite, requires two different steps. In order to understand the best strategy for the incorporation of neutral molecules into saponite, both methods were explored and a model molecule, the fluorene, is selected because it is cheaper than the neutral synthetic photoactive dye and it is easy to detect with optical spectroscopies. After the exhaustive characterization of the two hybrid fluorene-saponite samples, the LAG treatment was demonstrated to be the best one for the incorporation of neutral molecules. Hence, this method was applied for the incorporation into saponite of a neutral synthetic photoactive dye, called GAM2-35, that is an innovative novel neutral dye, having a good Stokes shift (185nm and 151nm, depending on the solvents), and it is quite cheap if compared to other synthetic dyes. The GAM_CTA_Sap_LAG was synthesized with LAG methodology and it was widely characterized, and finally was dispersed in Kurarity, a copolymer of PMMA and PnBA. After the incorporation into the inorganic support, the Stokes shift is lower than the dye alone because there is an overlapping between absorption and emission spectra. Conversely, the dispersion of composite in the Kurarity polymer enhances of 54nm the Stokes Shift, removing the overlap of the bands. Probably the extrusion delaminates the hybrid-saponite, increasing the dispersion of the dye molecules and decreasing the self-quenching effect.

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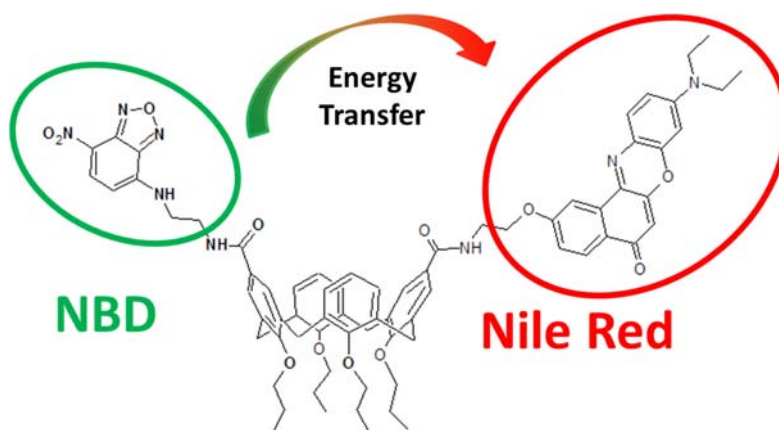
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P.17. Efficient energy transfer in hetero-bichromophoric calixarene systems

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Hetero-bichromophoric systems were prepared linking covalently Nile Red and NBD units to calix[4]arene scaffolds blocked in cone or partial cone structure. The two fluorescent dyes, NBD and Nile Red, have been chosen because of the good overlap between the luminescence spectrum of NBD (the energy donor) and the absorption spectrum of Nile Red (the energy acceptor). The proximity of the two dyes, an essential pre-requisite for efficient energy transfer, is ensured by the covalent link to the scaffold.



Steady-state fluorescence spectra of the derivatives clearly indicate the occurring of a very efficient energy transfer from the NBD chromophoric unit to the Nile Red unit.

A detailed conformational study was performed through the analysis of ¹H NMR spectra (the pattern of the calixarene aromatic signals in the ¹H NMR spectrum is diagnostic of the preferred conformation of calix[4]arenes in the cone structure).

The dynamics and efficiency of the excitation energy transfer process between the donor and acceptor units was investigated through ultrafast pump–probe spectroscopy.

Results suggest that the external medium strongly influences the conformation adopted by the bichromophores, with a direct effect on the extent of excitonic coupling between the dyes and hence on the dynamics of the energy transfer process itself.

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P.18. Synthesis of a calix[4]arene-based chromophore dyad for the study of photoinduced electron transfer

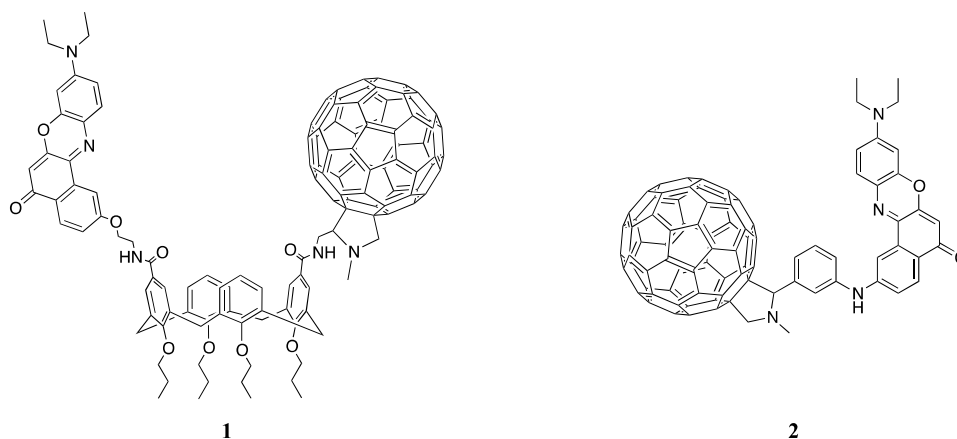
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In the last few decades organic solar cells (OSCs) have shown a great potential as low-cost sustainable energy sources with low environmental impact. Understanding the photoconversion mechanism is fundamental for the design of efficient OSCs.

In this context, our work is focused on the synthesis of a covalent electron donor-acceptor dyad as a model system for the study of the photoinduced electron transfer occurring between the two chromophores, 2-hydroxy Nile Red as the donor and fullerene C₆₀ as the acceptor. Nile Red is a well-known fluorescent and solvatochromic dye, which has been widely used as luminescent probe in the study of many chemical and biological systems and recently in the study of electron transfer with TiO₂ colloidal nanoparticles [1]. Fullerenes, on the other hand, are characterized by high electron affinity and require small reorganization energy in the electron transfer processes. In addition, the presence of fullerene in a donor-acceptor dyad is able to promote long-lived charge-separated states.

We anchored the two chromophores at the upper rim of a cone calix[4]arene (compound **1**), a convenient scaffold that allows the two moieties to be oriented in the same direction. Due to the residual flexibility of the structure, a modulation of the distance between the chromophores as a function of the medium could also be envisaged. A linear tri-components structure (**2**), composed of Nile Red-aromatic spacer-fullerene C₆₀ was also synthesized as a reference compound to study the influence of the calixarene scaffold on the electron transfer process.



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P.19. Hybrid photoluminescent dyes-silica nanoparticles: possible molecular control of the photophysical properties

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The photoemission brightness and stability of organic fluorophores can be significantly improved by the entrapment into silica nanoparticles. Independently of the fluorophore and the preparation method, the performance of the final nanomaterial is determined to a significant extent by the distribution of the photoluminescent molecules within the host matrix because intermolecular quenching effects can occur. In this respect, seminal works were carried out on Stöber dye-silica NP [1,2] where, unfortunately, the preparation easiness is not accompanied by a monodispersion of the NP size. However, siliceous hybrid NP highly homogenous in shape and size can be obtained by the microemulsion technique, where the NPs formation is ruled by the partition equilibria of the silica precursor (TEOS) and dye molecules between the oil and water phases, separated by the surfactant palisade of the reverse micelles. The multiphasic character of the reverse microemulsion stimulated in the investigation of the role of the hydrophilicity of a dye in determining its dispersion in the final hybrid NPs. In this respect, we investigated the dependence of photophysical performances on the relative affinity of TEOS and dyes molecules towards the water pool within the reverse micelles. Three cyanine dyes differing for number of sulfonic substituents, and then with a different hydrophilicity, were used. Systematic comparisons of the photophysical properties of the three dyes dissolved in the microemulsion, during the NP formation process and entrapped in the final NP demonstrated that the photoemission brightness, and then the dispersion of dye molecules within silica, increases as the fluorophore hydrophilicity decreases. It is proposed that such a dependence results from a decrease of diffusion rate toward the water pool in the reverse micelles with respect to hydrolyzed TEOS monomers, favouring the distribution of dye molecules in outer shells growing around undoped silica nuclei and subparticles.

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P. 20. Tailoring the surface properties of TiO₂: Shape Controlled Nanoparticles for the optimization of functional properties

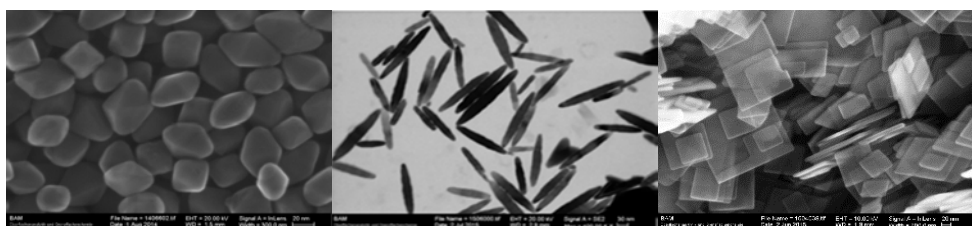
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The synthesis of TiO₂ nanoparticles (NPs) with well-defined morphology and size is fundamental for the development of advanced nanomaterials in various application fields: photocatalysis, photovoltaics, sensors, bone-implants with enhanced bone integration. Synthetic routes were developed for bipyramidal TiO₂ facet-controlled anatase NPs with low truncation along the c-axis and acicular morphology, through hydrothermal treatments of aqueous solutions of Ti(IV)(triethanolamine)₂ [1,2]. The formation of anatase (101) surfaces is favoured by the presence of OH ligands, including water. Therefore, the shape control agents used were pH and triethanolamine. Bipyramidal TiO₂ anatase NPs with low truncation along the c-axis and with dimensional polydispersity in the 5-20% range were produced, along with the procedure and the process parameters (pH, temperature and reagents concentrations) to modulate the NP size along the c-axis in the 20-60 nm range. Through a careful experimental design the influence of many process parameters (pH, temperature, shape controller type and concentration) on the synthesis outcome (size, shape and polydispersity), a predictive soft model was developed. The model is able to predict reasonably well the synthesis outcome. Synthesis of TiO₂ anatase nanoplatelets are carried out with a solvothermal synthesis using Titanium (IV) Butoxide [3]. Concentrated hydrofluoric acid as capping agents. The photocatalytic activity of the materials was studied in a gas-solid photoreactor for the NO degradation.



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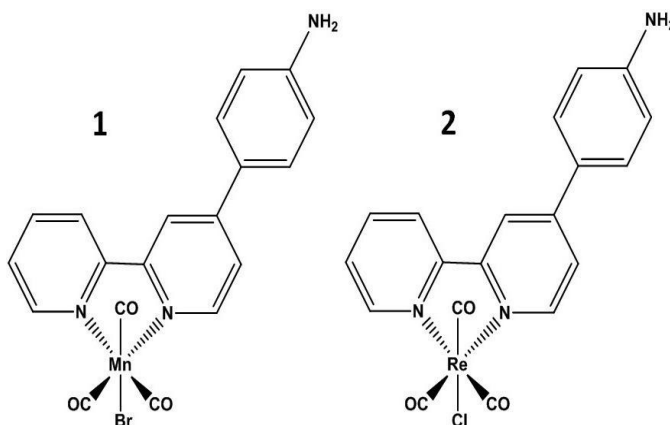
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P.21. Electrocatalysis by Mn^I and Re^I Organometallic Complexes for Homogeneous and Heterogeneous Electrochemical Reduction of CO₂

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Catalytic reduction of CO₂ is a great challenge for clean energy and environment.¹ In the research of CO₂ catalysts, homogeneous catalysis is favored for its easy operation but also suffers the downsides such as more deactivation in solution. A comparison between homogeneous and heterogeneous version of the same catalysts would let to point out advantages (and disadvantages) of the two approaches.² Here we report the electrochemical behavior of two new rhenium and manganese complexes, namely fac-Mn(CO)₃(L)Br (1) and fac-Re(CO)₃(L)Cl (2) (L = 4-(4-aminophenyl)-2,2'-bipyridine, both in homogeneous solution and covalently attached to glass carbon electrode (GCE) surfaces. The covalent bonding to GC surface was obtained by two approaches: 1) by oxidation of amino group or 2) by reduction of diazonium salts. The performances of the electrochemical reduction of CO₂ to CO in homogeneous and heterogeneous solutions were compared. Functionalized surfaces show about 60-fold increase in turnover numbers (TONs) within a much shorter time.



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P.22. Polythiophenes and C-doped carbon nitride: Towards a photo-assisted CO₂ reduction approach

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One important technological target in the near future is the conversion of solar energy into fuels: H₂ (by water splitting reaction) or carbon reduced species, from CO₂ fixing by artificial processes that mimic photosynthesis. Systems composed of stable semiconductors designed for H₂O oxidation and CO₂ reduction directly at their surfaces, functionalized with suitable catalysts, seem to be one of the best answers. Many surface catalysts able to carry out CO₂ reduction are metallorganic complexes. [1]

We functionalized a glassy carbon electrode (GCE) with Re(bpy-R)(CO)₃Cl, in which bpy-R is 4-(4-aminophenyl)-2,2'-bipyridine, a ligand conveniently designed to allow covalent bonding with GCE by an electrochemical grafting method, and not by simple physisorption. Then we tested the CO₂ reduction activity of the functionalized GCE and we observed that the grafted complex retained its activity with CO evolution under a bias application of -1.2 V vs Ag/AgCl. CO evolution was observed also on GCE/PEDOT/Re(bpy-R)(CO)₃Cl, nevertheless, the TON increase under irradiation was negligible, due to the scarce PEDOT photoactivity.

We also focused our attention on the synthesis of photoactive p-type semiconductors in order to functionalize them with the metallorganic catalyst tested, aiming at promoting the catalytic cycle with irradiation at significantly reduced external bias. There is a limited availability of organic p-type semiconductors with suitable energy band position to perform CO₂ reduction, high electronic conductivity, large density of photo-generated charge carriers and that easily undergo surface functionalization [2]. We therefore concentrated our efforts on the development of C-doped polymeric carbon nitride and modified polythiophene [3] photoelectrodes. We obtained materials with marked photoactivity, suitable energy band position and sufficient stability under the conditions of operation. The coupling with Re(bpy-R)(CO)₃Cl is still in progress.

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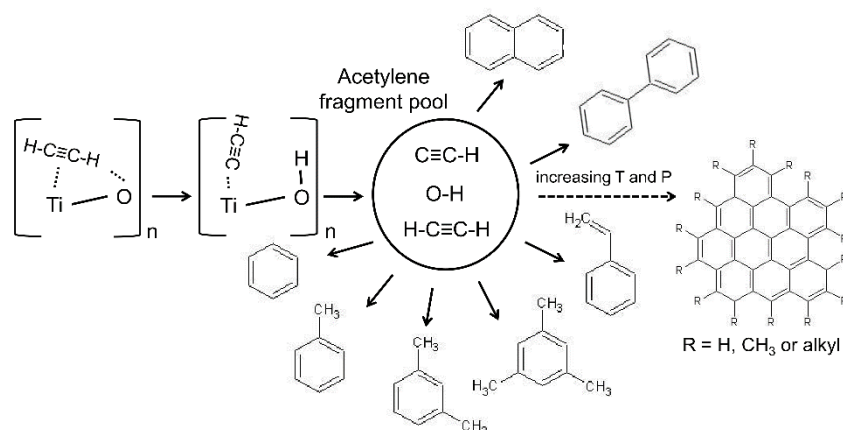
P. 23. Toward *in situ* growth of graphene on TiO₂ surfaces by C₂H₂ self-assembly

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Photoactive systems based on oxide semiconductors are widely studied for energy-related applications owing to their photo-stability, affordable cost and low toxicity. However, a further improvement of their efficiency is needed to promote large-scale applications: this has been attempted by doping with metal and non-metal impurities or by coupling different oxides. In this context, metal oxide/graphene composites have recently attracted increasing attention due to their high electron conductivity, large surface area and good adsorption properties. Various methods have been developed for the synthesis of graphene, including mechanical exfoliation, epitaxial growth and reduction of graphite oxide.

Only few studies explored the possibility to directly grow graphene *in situ* on the oxide surface using a bottom-up strategy. In our contribution we show that *in situ* acetylene oligomerization is an effective way to obtain polycyclic condensed hydrocarbons in close contact with the TiO₂ surface (see Figure below). These products can represent intermediate steps toward the *in situ* synthesis of graphene layers on TiO₂ in very mild conditions, allowing to avoid the anatase to rutile transformation. The reaction has been monitored by IR and UV-vis spectroscopies and by continuous wave Electron Paramagnetic Resonance (CW-EPR).¹⁻² Density functional theory (DFT) calculations³ show that acetylene is physisorbed on the anatase (101) surface without activation of the C-H bond. On the contrary, the dehydroxylated (001) anatase surface is very active and leads to the spontaneous splitting of the C-H bond and to the cyclo-oligomerization of the monomer.



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P. 24. Facile synthesis of NIR and Visible luminescent Sm³⁺ doped lutetium oxide nanoparticles

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The Rare Earth based compounds such as oxides, carbonates and dioxycarbonates [1,2], are widely studied for their peculiar properties and for the potential applications in bioimaging techniques [3]. In the recent years, several studies have been focused on the lutetium based compounds in the oxidic form, that is a favorable matrix for lanthanide ions insertion and possesses interesting physical chemistry properties such as phase stability and high melting point. Lu₂O₃ properly doped has been studied as a bioimaging probe, up-conversion phosphor, single crystal, glass and transparent film and luminescent phosphors. Ln³⁺ (Ln= Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) doped Lu₂O₃ compounds have been resulted attractive compounds [4]. A series of Sm³⁺ doped Lu₂O₃ nanoparticles have been synthesized via a simple co-precipitation method using oxalic acid as precipitant. The obtained compounds showed a platelet-like morphology with diameter ranging between 10 and 14 nm. Sm³⁺ doped Lu₂O₃ nanoparticles showed interesting visible and near infrared emission, which was carefully evaluated together with lifetime measurements. In particular, the system with the lowest Sm³⁺ loading exhibited the best photoluminescence performances [5]. The potential toxicity of the optimized system (Lu₂O₃:Sm1%) was preliminarily evaluated in human endothelial cells (HECV), observing a significant loss in cell viability only above the concentration of 1 µg/ml. To our knowledge, these represent the first data on cytotoxicity of Lu₂O₃ nanoparticles in human cells. The small dimensions, the capability to emit in the NIR region and the absence of toxicity in diluted suspension, candidate Lu₂O₃:Sm1% as potential luminescent probe in bioimaging technique.

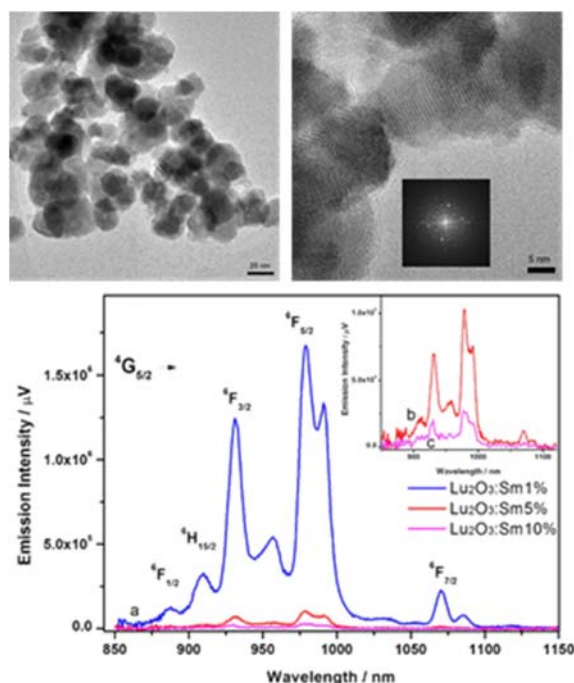


Figure 1 HRTEM images (upper section) and NIR luminescence (lower section) of Sm³⁺ doped Lu₂O₃ nanoparticles.

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P.25. Organization of photoactive azobenzene molecules inside AlPO₄-5

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The regular pore systems of nanometric openings exhibited by zeolite frameworks make these porous materials ideal host matrices for achieving supramolecular organization of photoactive species¹⁻³. Organic/inorganic hybrid materials (like zeolites+colorants) are currently used in strategic areas, from sustainable energy technologies to biomedical sciences. In these systems, photoactive molecules are organized in one-dimensional nanostructures inside the zeolite channels⁴. It is known that the properties of the hybrids depend on the packing of molecules inside the channels, which controls the intermolecular interactions and the interactions of the dyes with the framework. Studies on zeolites with AFI topology demonstrated the incorporation and the linear alignment of dyes into AlPO₄-5, new spectroscopic properties are observed and the results indicate laser action in the system with properties tunable over a wide range⁵⁻⁹. However for these systems, detailed information on the crystal structure and on the host/guest interactions are completely lacking.

AlPO₄-5 (s.g. P6cc, $a=b=13.827$ Å, $c=8.580$, $V=1420.64$ Å³) is characterized by 12-ring channels with free diameter of 0.73 nm. The AlPO₄-5 samples were synthesized with the following molar composition of the synthesis gel: 1Al₂O₃ : 1.33P₂O₅ : 0.6 TEA : 100H₂O. The gel was heated at 210°C for 4 days. The as-synthesized sample was calcined and mixed with azobenzene in a ratio corresponding to loading of 1.0 molecule per unit cell and heated at 115°C for 24 h. The final loaded composites had a mustard color.

The calcined AlPO₄-5 and the composite were analyzed by synchrotron XRPD on the beamline ID22 at ESRF (Grenoble) and the X-Press beamline at Elettra Synchrotron Trieste, respectively and by thermogravimetric analyses. The structural refinements were performed by Rietveld profile fitting.

The TG curves show that a portion of the water molecules present in the calcined sample (weight loss 18%, corresponding to 18 water molecules p.u.c.) is substituted by the dye-molecules. The determined dye content is 0.9 molecules p.u.c.

The structural refinements shows that the penetration of azobenzene influences the cell parameters (increase of a and b , decrease of c). Azobenzene molecule is confined in the 12-ring channels and is tilted of 36° with respect to the channel axis. These results, in agreement with other data reported in literature⁹, indicate that there is a structure-directing influence of the host on the guest molecules, in dependence of their size. The effects of the interactions between the dye molecules and the zeolite framework on the electronic states will be examined by IR, diffuse reflectance UV–visible absorption and fluorescence emission.

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