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The power of intermolecular interactions in organic semiconductors: from threaded molecular wires to P3HT nanofibres and PCBM single crystals

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Over the last 40 years the versatility of organic chemistry has allowed significant progress in achieving control over the solid-state properties of functional organic molecules, the attention being focused especially on covalent bonding and on tailoring of "intramolecular functionality". Control at the intermolecular level is more elusive, but still crucial for manipulating and optimising relevant properties of the functional materials, such charge transport or luminescence. Threaded molecular wires made with conjugated-polymers-based polyrotaxanes offer an example of a "bottom-up" approach to electroluminescent nanostructures incorporating supramolecular design concepts.[1] Namely, this class of materials is engineered at a supramolecular level by threading a conjugated macromolecule, such as poly(para-phenylene), poly(4,4'-diphenylene vinylene) or poly(9,9'-fluorene) through α - or β -cyclodextrin rings, so as to reduce solid-state packing effects that red-shift and partially quench the luminescence. Such a supramolecular approach preserves the fundamental semiconducting properties of the conjugated wires, and is effective at both increasing the photoluminescence efficiency and blue-shifting the emission of the conjugated cores, in the solid state, while still allowing charge-transport and thus electroluminescence (EL). The reduced tendency for polymer chains to aggregate shows in both solid-state films and in solution (as probed by fluorescence decay dynamics) and allows solutionprocessing of individual polyrotaxane wires onto substrates, as revealed by scanning-force microscopy.[2] Further control of the optical and morphological properties of these materials is enabled by their polyelectrolytic nature that allows the synergistic exploitation of ionic secondary interaction, via tailoring of the counter-cations size. Control of the threading ratio is also possible, thereby resulting in fine tuning of the excitonic vs. aggregate contribution to the luminescence, as well as of the electro- and photo-luminescence efficiency.[5] An intriguing possibility afforded by supramolecular and nanoscale encapsulation of these soluble semiconductors is the suppression of energy transfer which enables both fabrication of white-emitting LEDs,[6] and achievement of unprecedentedly broad gain bands, in "conjugated" blends of different semiconductors, with potential application to broad-band amplifiers and multi-colour lasers.[7] Water solubility of rotaxanes carrying un-substituted cyclodextrins also enables their incorporation into stretchable matrices and thus strong polarisation of absorption and emission from such films.[8]

Whereas design of materials for luminescent application is generally aimed at partial or total suppression of intermolecular interactions, and in particular of pi-pi stacking, applications relying primarily on charge transport such as field-effect transistors (FETs) and photovoltaic diodes (PVDs) require optimisation of charge mobility, which is favoured, in turn, by strong intermolecular interactions and tight packing, as common in crystalline structures. In the second part of the talk I will present results on poly(3-hexylthiophene-2,5-diyl) (P3HT)-based nanofibres whose optical and transport properties are also strongly influenced by intermolecular interactions through enhanced cristallinity (compared to non-nanostructured films).[9] Finally, I will conclude by reporting the recent preparation and characterisation of solvent-free, high-quality and large (100s of micrometers) single crystals of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).[10]

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Organo-lead Tri- Halides Perovskites for Highly Efficient Solar Cells: Photophysical versus Structural Properties

Annamaria Petrozza

Here we present a comprehensive picture of the main photophysical properties of methyl ammonium lead tri-iodide perovskite $(CH_3NH_3PbI_3)$ and its Chlorine-doped counterpart (Cl-doped $CH_3NH_3PbI_3$) with a particular focus on the structure-optical properties relationship, emphasizing the role of the interfaces from a molecular to mesoscopic level. By combining optical, vibrational, and structural studies we investigate time scale and dynamics of carriers thermalization, state filling effect, band gap renormalization, exciton formation , and ionization and we correlate them to the thin film morphology.

Solar Electricity and Fuels: a A-to-Z Molecular Hybrid and Organic Approach

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Energy from Sun in modern society implies both electricity and fuels. With this target in mind we have developed in the last years a multidimensional approach, from molecular design to device, based on hybrid and organic materials.

Our studies on organometallic and organic sensitizers,¹⁻³ iodine-free and quasi-solid electrolytes,⁴ nanostructured TiO₂⁵ will be presented. In particular we have introduced in the last years a new design approach for metal-free sensitizers, now widely used in the DSSC community, based on a multi-branched geometry, for improved light harvesting and enhanced stability compared to the conventional linear D- π -A sensitizers.¹ We will also present our most recent results on multi-branched dyes for solar-induced hydrogen production from water.

In the last part of the lecture a few slides will be dedicated to the introduction of Ener*CHEM*, the recently established group of the Italian Chemical Society on Chemistry of Renewable Energies, whose members come for the diverse areas of research on renewable energy materials and devices in Italy.⁶



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Large area perovskite photovoltaic modules

Aldo Di Carlo

In this work we exploit the use of a new promising class of light harvesting materials, namely the hybrid organic halide perovskites (CH3NH3PbI3-xClx), for the fabrication of series-connected monolithic perovskite modules. To achieve this goal, important innovative procedures were implemented in order to define a reproducible fabrication path applicable to large area devices. The first attempt to fabricate modules, with both Spiro-OMeTAD and the P3HT polymer as Hole Transporting Material (HTM), showed a Power Conversion Efficiency (PCE) of 5.1% on an active area of 13.44cm2. In order to improve the efficiency of the module, we developed a new Laser assisted patterning of the perovskite/compact layers together with an optimized perovskite deposition in controlled atmosphere. This allowed us to improve the module PCE up to 13% on 10 cm2 which represent the state of art efficiency for a perovskite module. At the same time, printing techniques have been adapted to deposit perovskite materials on larger areas. A 100 cm2 module have been obtained with a 4.5% efficiency

Direct observation of ultrafast long-range charge separation at polymerfullerene heterojunctions

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In polymeric semiconductors, charge carriers are polarons, which means that the excess charge deforms the molecular structure of the polymer chain that hosts it. This results in distinctive signatures in the vibrational modes of the polymer. Here, we probe polaron photogeneration dynamics at polymer:fullerene heterojunctions by monitoring its time-resolved resonance-Raman spectrum following ultrafast photoexcitation. We conclude that polarons emerge within 300 fs. Surprisingly, further structural evolution on < 50-ps timescales is modest, indicating that the polymer conformation hosting nascent polarons is not significantly different from that near equilibrium. We interpret this as suggestive that charges are free from their mutual Coulomb potential because we would expect rich vibrational dynamics associated with charge-pair relaxation. We address current debates on the photocarrier generation mechanism at molecular heterojunctions, and our work is, to our knowledge, the first direct probe of molecular conformation dynamics during this fundamentally important process in these materials.

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New bulk heterojunctions for organic photovoltaics

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Formation of charge carriers at the donor acceptor interface, after optical absorption in organic molecules and polymers forming bulk heterojunctions, is crucial in order to form high efficiency organic photovoltaic devices. Such donor/acceptor interfaces have many forms. Some recent improvements in polymer/polymer heterojunctions and in donor molecule/acceptor polymer are reviewed. Improved optical absorption in thin films is the common theme, now accomplished by substituting a weakly absorbing fullerene acceptor with alternative acceptor polymer with desirable optical characteristics. These fullerene free blends also reduces the energy input in the synthesis of the bulk heterojunction, thus considerably improving the energy pay back time of materials in devices.

The power of materials science tools for gaining insights in organic optoelectronic devices

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In the past decade, significant progress has been made in the fabrication of organic optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) or organic photovoltaics (OPVs), predominantly due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist. In the field of OPVs, real understanding of what structural and electronic features determine, for instance, the short-circuit current (Jsc), open-circuit voltage (Voc) and fill factor are still lacking; and the role of charge transfer states and which charge transfer states are critical for efficient charge generation is still heavily debated. Here we attempt to obtain further insight of relevant structure/ processing/ performance interrelations using classical polymer processing 'tools'. We present a survey on the principles of structure development from the liquid phase of this material family with focus on how to manipulate their phase transformations and solid-state order to tailor and tune the final 'morphology' towards technological and practical applications, and establish correlations with relevant device characteristics. This will include the interrelation of intermixed phase with charge transfer absorption, how we can manipulate the charge transfer energy and what structural features seem to influence Voc. Similar aspects in the OFET field will also be addressed.

Photonic structures for light trapping in thin-film solar cells

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Light trapping is crucial to increase efficiency in thin-film solar cells and to reduce the cost of advanced photovoltaic devices. It is especially important to enhance light absorption in the spectral region close to the electronic band gap of the semiconductor, where material absorption is low – and to approach the ultimate limit to absorption, which is usually taken to be the Lambertian limit given by a fully randomizing light scatterer. At the same time, high energy conversion efficiency requires good carrier collection, which should not be compromised by the presence of patterned or rough interfaces.

In this work we report on a theoretical study of thin-film silicon solar cells with various types of ordered, disordered, and hybrid photonic structures at the wavelength scale of light in the visible spectrum. Light trapping capabilities of these systems are analyzed by means of rigorous coupled-wave analysis [1,2] and compared with the Lambertian limit. The best photonic structures are found to require proper combinations of order and disorder, and can be fabricated with top-down processing techniques.

Carrier collection is studied by solving drift-diffusion equations by an analytical model in the presence of Lambertian light trapping, and by means of full electro-optical simulations with the finite-element method (Silvaco-ATLAS software) [3,4]. The results indicate that thin-film silicon solar cells can be more efficient than bulk ones with comparable material quality, provided light trapping close to the Lambertian limit is achieved and surface recombination is kept below a critical level, which is compatible with present surface-passivation technologies. The optimal c-Si thickness is in the 20-30 micron range.

These results suggest that a new generation of thin-film silicon solar cells with efficiencies comparable to present wafer-based solar cells is a challenging, but realistic goal. Recent progress in the fabrication of high-quality, non wafer-based thin c-Si layers is very promising in this context.

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Modeling Materials and Processes in Hybrid/Organic Photovoltaics: From Dye-sensitized to Perovskite Solar Cells

FILIPPO DE ANGELIS

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Dye-sensitized solar cells (DSCs) have maintained a clear lead over competing hybrid/organic photovoltaics technologies for about two decades. In 2012, the first reports of high efficiency solid-state DSCs based on organohalide lead perovskites completely revolutionized the field. These materials are used as light-absorbers in DSCs and as light-harvesting and electron conductor in meso-superstructured and flat heterojunction solar cells and show certified efficiencies that exceed 17%.

Relevant advances in the DSCs field have relied on the computational design and screening of new materials, with researchers examining material characteristics that can improve device performance and/or stability. Suitable modeling strategies allow researchers to observe the otherwise inaccessible but crucial hetero-interfaces that control the operation of DSCs, allowing researchers the opportunity to develop new and more efficient materials and optimize processes.

A unified view of recent computational modeling research examining DSCs will be presented, illustrating how the principles and simulation tools used for these systems can be adapted to study the emerging field of perovskite solar cells. We illustrate the performance of the proposed simulation toolbox along with the fundamental modeling strategies using selected examples of relevant isolated device constituents, including dyes/perovskite absorbers, metal-oxide surfaces/nanoparticles, and hole transporters, and their heterointerfaces. We critically assess the accuracy of various computational approaches against the related experimental data and analyze the representative interfaces that control the device operational mechanism.

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Hybrid photoconverters from molecular dyes and photosynthetic bacteria

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Artificial photosynthetic systems capable of harvesting solar light for energy production and photocatalysis have attracted considerable interest over the last years.

As a possible approach to such functional architectures we propose combination of tailored molecular antennas for effective and tuneable light harvesting with biological photoconverters optimized by billion years of evolution.

The lecture will present the synthesis of hybrid bio-organic photoconverters by covalent functionalization of the Reaction Center (RC) photoenzyme from the photosynthetic bacterium *Rhodobacter sphaeroides* R26 with tailored molecular fluorophores (figure). The organic fluorophore acts as the antenna to enhance the light harvesting capability of the RC in a wavelength range where the unmodified biological enzyme does not absorb¹.

Various dyes have been synthesized with bis-thiophene benzothiadiazole or bis-thiophene thiazoloquinoxaline core and have been covalently bound to selected positions of the RC photoenzyme. We have also demonstrated selective functionalization for anchoring the photoenzyme on graphene or embedding it into membranes, aiming to integrate the photoactive units into photoelectrodes and electronic devices.

Our study shows that it is possible to design and synthesize organic-biological hybrid photosynthetic assemblies for solar energy conversion. The resulting bio-hybrids outperform the native photoenzyme in light harvesting and conversion ability. New concepts for the generation of materials for sunlight photoconversion can be envisaged.



Figure: The photosynthetic Reaction Center and the antenna dye

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Industrial development of large area thin film modules: perspectives for increasing the power conversion efficiency and reducing costs

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Inorganic thin-film solar cells have made a lot of progresses during the past decade and have stimulated great research and commercial interest.

Among thin film technologies a-Si/mc-Si based technologies are manufactured at low costs and exhibit both high reliability and good performances for large field applications. On the other hand CdTe and CIGS show higher potential to increase the power conversion efficiency.

However, in the last two years the fast decrease of crystalline silicon solar cells prices has made thin film technology even more challenging. To survive in the tough competitive environment thin film efficiency at module level has to be raised well above the current performances in the next few years, with even more competitive costs. We will discuss on the activities aimed at increasing the efficiency, reducing the manufacturing costs and ensuring long term reliability.

Moreover, we will discuss about the future outlooks of thin film technology, including the development of solution-processed hybrid inorganic-inorganic, or organic-inorganic, heterojunction solar cells, which could have the potential to significantly increase the thin film modules efficiency maintaining or even reducing the fabrication cost.

TCO free Bulk heterojunction solar cells with nanostructured graphene electrodes

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Organic solar cells (OSCs) have attracted considerable interest in the last years due to their potential application in low-cost and large-area production. The typical structure of a BHJ-SC consists on an active layer that is a blend of p and n materials, sandwiched between two electrodes, a transparent conductive oxide (TCO) and an evaporated metal. The TCO mainly used is indium tin oxide (ITO) which unfortunately presents serious issues related to i) the release of oxygen and indium into the organic layer, ii) the poor transparency in the blue region, iii) its stiffness, which prevents its use in flexible solar cells, and iv) the large cost due to the limited supply of indium. Several candidates have been reported to replace ITO, such as conductive films based on carbon nanotubes (CNT) or graphene. The limited thermal and chemical stability and the high surface roughness of CNT films, make this option less desirable. In this context the use of graphene as semitransparent electrode has been proposed and photovoltaic devices have been already demonstrated also for flexible substrates. In this presentation we propose an approach in which the graphene electrode is 3D structured and acts not only as a contact, but also as photonic crystal. We simulated several solar cell architectures considering different materials, such as PEDOT:PSS or MoO₃ as hole transporting layer (HTL) and P3HT:PCBM or PTB7:PC70BM as active layer. The study has been performed using an electromagnetic simulator permitting the calculation of absorbed photons in the active layer for any geometrical configuration. We optimized the grating structure demonstrating an enhancement of the optical absorption up to 27% respect to a flat solar cell with same active layer thickness.

We report also the fabrication of organic solar cells with a multi-layer graphene as semitransparent electrode. The multilayer graphene was grown by rapid thermal annealing on nickel films using a solid carbon source and transferred to glass substrates using a wet chemical transfer method. The obtained devices have been characterized in terms of optical and electrical characteristics reaching a preliminary maximum efficiency of 1,5% with two different HTL (PEDOT:PSS and MoO3) and P3HT:PCBM as active layer. This efficiency, which is strongly affected by the quality of the graphene contact that reached a minimum sheet resistance of $3K\Box/\Box$, is about half of the efficiency achieved with the standard TCO based structure (~3%).

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Engineering Colloidal Nanocrystal Surface for Photovoltaics

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In the search for high-efficiency and cost-effective solar cell solutions, wet-chemically prepared nanocrystals (NCs) have also drawn much interest.[1] NCs can be seen as a semiconducting ink and their absorption can be tuned across the visible and, most importantly, up to the NIR region to mirror and harvest the solar spectrum. Engineering NC surface plays a major role for their integration in highly efficient photovoltaic device;[2] through surface modification we can indeed tune their opto-electronic properties and we can exploit their self-assembly and packing properties to form a dense solid semiconductor material at low or even room-temperature.

In our work we explore different nanocrystalline materials, form infrared absorbing lead sulfide (PbS) to titanium dioxide (TiO₂) NCs, as key functional components into solar cell devices by means of mild, all-solution-based processing techniques.[3,4] To this aim we have developed *ad hoc* modification or removal of insulating capping ligands from NC surfaces in both solid-state and liquid-phase conditions. We propose all-inorganic hetero-structured junction devices made of PbS NCs as absorber and TiO₂ NCs as electron acceptor species. All the device fabrication procedures rely on room-temperature processing, which is compatible with flexible plastic substrate and low-cost production.[3-5]

Finally we profit by NC surface engineering to develop photoactive hybrid nanocomposites obtained upon blending conjugated polymers and NCs. We demonstrate that tailoring NC surface chemistry permits to control non-covalent and electronic interactions between organic and inorganic components. We show that the pending moieties of organic ligands at the nanocrystal surface do not merely confer colloidal stability, but drastically impact morphology and interfaces of hybrid composites during formation from blend solutions. The feasibility of our approach in photovoltaic applications is demonstrated for composites based on poly(3-hexylthiophene) and PbS NCs, considered as inadequate until this report, which enable the fabrication of hybrid solar cells displaying a power conversion efficiency that reaches 3 %.[6]

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Synthesis and characterization of a low band-gap random copolymer based on benzotriazole and benzothiadiazole moieties for bulk hetero-junction solar cells

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In the last twenty years, semiconducting polymers have attracted a great interest as absorbing materials in optoelectronic devices. Recent literature¹ has highlighted the importance of conventional cross-coupling reactions (e.g. Stille coupling) in the synthesis of most performant copolymers for BHJ solar cells; however, conventional cross-coupling reactions are generally not suitable to scale-up for production of semiconducting polymers.

In this context, DHAP (Direct Hetero-Arylation Polymerization) appears a very attractive synthetic tool for organic chemists since it does not involve the use of organometallic intermediates². In our recent review³ we have emphasized, from an industrial perspective, the simplicity and the effectiveness associated to the direct arylation protocols not only in terms of reduction of the synthetic steps but especially in view of easier recoverability of the polymers from reaction byproducts.

We report herein the synthesis of a double acceptor ternary random copolymer based on benzotriazole and benzothiadiazole as the accepting units and benzodithiophene as the donor moiety (Figure 1) by means of direct arylation polycondensation. This polymer was already reported in a previous work⁴ where it was prepared via the Stille coupling reaction to afford a material with PCE of 5% in an optimized solar cell device.

Preliminary experimental results dealing with molecular weight distributions and polydispersity indexes of the final materials will be discussed emphasizing the differences between Stille and DHAP protocols.

POLYMERIZATION PROTOCOL



Figure 1

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Enhancing dye-sensitized solar cell performances by fine molecular engineering

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The communication will deal with the synthesis and characterization of two \Box -extended organic sensitizers for applications in dye-sensitized solar cells. The materials are designed with a D-A- π -A structure constituted by *i*) a triarylamine group as donor, *ii*) a dithienyl-benzothiadiazole chromophore followed by *iii*) a further ethynylene-thiophene (G1) or ethynylene-benzene (G2) \Box -spacer and iv) a cyano-acrylic moiety as acceptor/anchoring region. An unusual structural extension of the \Box -bridge singles out these structures.



In DSSC devices, a superior power conversion efficiency of G2 8.1% with respect to G1(6.0%) could be obtained although in the presence of a relatively high CDCA amount, necessary to ease their aggregation tendency.

The UV-vis spectrum of **G2**, is characterized by a "camelback" profile, which leads to an absorption loss between 400 and 500 nm. Therefore, starting from **G2** the **DTB-B** and **DTB-T** have been designed to be used as specific co-sensitizers.



The co-sensitizers exhibited highly planar structures and an absorption spectrum complementary to that of the main sensitizer. In fact, when suitably used as dyes in mixture with **G2**, **DTB-B** and **DTB-T** promoted a sensible light-harvesting improvement. The specific structural tailoring of the co-sensitizers seems to induce a synergy with **G2**, leading to an efficiency higher than the sum of those recorded for individual dyes.

The results indicate that \Box -bridge extension is a viable strategy to improve dye efficiency and suggest analogous structural engineering of known low band-gap sensitizers as a promising approach to push forward the efficiency of DSSCs.

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Optical Limitations of Thin-Film Perovskite-Based Solar Cells

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Perovskite light-harvesters have rapidly emerged to the forefront of photovoltaics research exhibiting high power-conversion efficiencies and the promise of low-cost fabrication in devices. Despite recent progress in describing the internal mechanisms for photocurrent generation in perovskite solar cells, a full understanding of the device operation still requires an optical analysis of the device stack. This provides a platform for maximising the power-conversion efficiency through a precise determination of parasitic losses caused by optical coherence and absorption in non-photoactive layers. Here we present a transfer-matrix model for the charge-generation profile under sunlight in state-of-the-art perovskite-based planar-heterojunction solar cells using experimental refractive index data from spectroscopic ellipsometry. Excellent agreement between the model and experiment is obtained and reveals some important features of device operation. In particular, we find the optimum thickness for photocurrent generation, an accurate presentation of the wavelength dependence of the internal quantum efficiency, and the dependence of the photocurrent on incidence angle. In the latter case, we find that perovskite-based solar cells can compete favourably with conventional technologies not only at normal incidence but also throughout the daylight cycle. This work provides important insights into device optimisation which should lead to further improvements in device efficiency.

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Development of heterocyclic D- π -A dyes for application in efficient and stable thin-layer Dye Sensitized Solar Cells

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In recent years, our research activity has been mainly focused on the design and synthesis of new organic dyes, featuring different heterocyclic groups, with potential applications as DSSC sensitizers. In general, the compounds prepared in our laboratories were based on the classical D- π -A architecture, with a donor and an acceptor moiety joined by a conjugate spacer.^[1] We have explored the possibility to introduce different structural units in all three sections of the molecules (see Figure), aiming to improve their light absorption properties as well as their photochemical and anchoring stability, with the final objective to obtain more efficient and stable devices even under simple fabrication conditions. For example, we have introduced dyes featuring a thiazolo[5,4-*d*]thiazole central unit,^[2] and demonstrated that they can attain up to 7.71% efficiency in thin-layer, transparent DSSCs.^[3] Furthermore, we have synthesized compounds bearing pyridine-carboxylic acids and pyridine-*N*-oxides as anchoring groups, and demonstrated their superior anchoring stability compared to their cyanoacrylate-based counterparts.^[4]

In this communication, we will present the synthesis of our latest compounds, and discuss how structural modifications influence their optical properties as well as the stability of their attachment to TiO_2 . In addition, we will present our studies on the fabrication and testing of DSSCs built using the new sensitizers, highlighting our best results both in terms of device efficiency and stability.



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Synthesis and application of pheripherally functionalized organic additives for BHJ solar cells

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Aliphatic thiols and dithiols are processing additives for bulk heterojunction (BHJ) polimer solar cells that enables substitution of the post-production treatment with low energy processes (1). Additives improve the solubility of donor: acceptor couple in the host solvent, affecting solid state nanoscale phase separation. After deposition, thiol solvent is evaporated from the blend.

In this communication, we present the sulphur peripheral functionalization of conjugated structures as an effective way of tailoring properties of the third components for ternary blend (2) polymer solar cells. Such materials could not only optimize the active layer morphology but contribute, by means of their conjugated structure, to light harvesting and charge generation processes operating in the solar cell.

Building on our experience in the synthesis of thiol-functionalized materials (3), we recently synthesized a family of organic semiconductors with push-pull structure and pending alkylthioacetyl groups. In particular, a novel thiophene-benzothiadiazole-based small molecule with peripheral thioacetyl groups (**4T1BSAc**, Figure 1) was easily synthesized by palladium-catalyzed Suzuki-Miyaura coupling reaction. When this molecule was incorporated as the third component in a P3HT:PCBM BHJ solar cell, a significant improvement in the short circuit current density (Jsc) was achieved, resulting in a higher power conversion efficiency with respect to the pristine P3TH:PCBM device. When compared to its *n*-hexyl-terminated analogue (**4T1B**, Figure 1), the devices incorporating 10wt% of **4T1BSAc** exhibited 3.66% as the highest efficiency compared to 3.56% of the device incorporating 5wt% of **4T1B** with respect to P3HT. This increase (more than 20%) relative to the reference cell without additive ($\Box = 2.94$) is enhanced by the presence of the peripheral thioacetyl groups that improve the solubility of the compound and its compatibility with the blend components (4).



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Flexible dye-sensitized solar cell combining light-cured polymer network , metallic grids and vertically aligned TiO2 nanotube array

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Dye Sensitized Solar Cells gathered a widespread attention for the potential development of a very low cost photovoltaics, with versatile applications spamming from architectural integration to wearable photovoltaics and supply systems for low power electronics. However, some critical issues still have to be faced: the best performing DSCs are based on a rigid housing with glass/FTO electrodes, and steps towards the development of flexible devices have to be engaged. Moreover, the use of a liquid electrolyte is particularly critical, casting shadows on the possible durability of the device. During recent years we deepened a promising approach for the fabrication of quasi solid DSCs with excellent long-term durability. We thoroughly studied and characterized the integration of self standing polymeric membranes prepared by free radical photopolymerization, investigating different polymeric formulations. Very recently, this electrolytic system was integrated with an innovative design for DSC photoanode, based on the use of semitransparent metallic grids as a support for the sensitized nanostructured semiconductor. For photoanode fabrication, both the use of TiO₂ nanotubes directly grown on bendable Ti mesh and the deposition of mesoporous layers of TiO2 nanoparticles were investigated with excellent results. The main advantage of this solution is the possibility to perform the high temperature sintering process (which is mandatory for a well performing semiconductor layer with good electron transport properties) before the integration on the final polymeric housing of the cell.

We will illustrate our most recent results on the fabrication of fully flexible solar cells with metallic mesh-based anode and cathode, separated by a polymeric membrane charged with a I-based redox mediator. The electrochemical characterization of the transport properties of the device and a physic-based modeling of the system were developed. This kind of architecture satisfies the main requirements that a DSC has to fulfill: it is TCO-free, transparent, highly bendable and adaptable to complex shapes, and fabricated only with very low cost materials and with a simple and scalable technology.

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Elusive presence of chloride in hybrid halide perovskites

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Hybrid halide perovskites represent one of the most promising solutions toward the fabrication of all solid nanostructured solar cells, with improved efficiency and long-term stability. The role of chloride in the MAPbI3-xClx perovskite is still limitedly understood, albeit subjected of much debate. Here we report on a combined study including experiments and theory aiming to determine both the composition and the location of the chloride within the perovskite film, and correlate them with their photovoltaic performances.

We found out that, independent of the components ratio in the precursor solution, Cl incorporation in an iodide-based structure, is possible only at relatively low concentration levels (below 3–4%). Angle Resolved X-ray photoelectron spectroscopy (AR-XPS) were carried out on ad-hoc designed bi-layers of MAPbI3-xClx perovskite deposited onto a flat TiO2 substrate and reveal that the chloride is preferentially located in close proximity of the perovskite/TiO2 interface. DFT calculations indicate the preferential location of chloride at the TiO2 interface compared to the bulk perovskite, due to an increased chloride-TiO2 surface affinity. Furthermore, the calculations clearly demonstrate an interfacial chloride-induced band bending, creating a directional "electron funnel" which may improve the charge collection efficiency of the device, and possibly affecting also recombination pathways.

Our findings represent a step forward to the rationalization of the peculiar properties of mixed halide perovskite, allowing to further address material and device design issues.

Understanding and Design Hybrid Perovskites for Photovoltaics by atomistic simulations

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Hybrid perovskites $(CH_3-NH_3)PbI_{3-x}Cl_x$ combining organic molecules (methylammonia CH_3-NH_3) with inorganic perovskites of the ABO₃ type have been the rising-star materials of the latest and most promising frontier in photovoltaics developments. Solar cells based on $(CH_3-NH_3)PbI_{3-x}Cl_x$ as photon absorber, grown by inexpensive printing techniques reached record-high 15% efficiency. Impressively, in some experiments these hybrid perovskites were acting efficiently as both optically active and both n- and p-type transport material.

Our study unveil the most relevant sources of this excellent performance, i.e. large absorption coefficients (0.03-0.04 nm⁻¹ for wavelength ~500 nm) and small electron and hole effective masses, in turn related to peculiar characteristics such as the direct gap between highly dispersed Pb(6s)-I(5p) valence bands and Pb(6p) conduction bands.[1]

Luminescence properties and long lifetimes are explained in terms of simple minority carrier lifetime models and direct band-to-band recombination.

Additionally we calculate the current-voltage characteristic for ideally perfect crystalline perovskites and we discuss the possibility of further improving the photovoltaic parameters and functionalities of state-of-the art materials by a better control of defects.[2]

This understanding prefigures simple design rules to search for more hybrid perovskites with enhanced capabilities or specific requirements, such as the Pb replacement with non-toxic cations. The flexibility of the perovskite structure, which counts literally thousands of different materials, represents an ideal template for testing the widest range of atomic and molecular substitutions. The role of hybrid interactions in lead halide perovskite (CH3NH3PbI3) is further analyzed by discussing an effective interatomic potential for the simulation of large scale systems at finite temperature.[3]

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Optimization in Dye Sensitized Solar cells: a multiparametric approach.

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In recent years the research on Dye-sensitized Solar Cells (DSCs) has focused on the understanding of the photovoltaic processes and the improvement of the photoconversion efficiencies, currently around 12-13%¹. Despite these continuous advances, DSCs are not yet commercialized on large-scale, because they suffer of troubles in long-term stability, especially with organic and NIR sensitizers. In fact, the cells are subjected to undesirable phenomena, *i.e.* photodegradation of the dye anchored on semiconductor, leakage of the electrolyte, diffusion of pollutants from the outside and corrosion of some components. Another problem is due to the difficulty in realizing devices able to guarantee high photovoltaic performances with reliable reproducibility. The reason is that the cells are assembled with different and heterogeneous layers, each one affected by intrinsic variability; moreover the layers influence each other and this increases exponentially in cells with large active area, like modules and panels for commercial applications.

The idea of the present work started from the need to identify all the factors by which the photoconversion processes may be influenced. For this reason, the research has been conducted with a chemometric multivariate approach (Design of Experiment, DoE) that allows to simultaneously evaluate multiple variables by reducing the number of the needed experiments, in order to understand and possible predict the synergistic/antagonistic effects, due to the interactions between the variables themselves. Starting from some case studies recently published^{3,4} here we will describe in specific the development of a method that enabled us to study the photostability and the photovoltaic efficiency of a series of NIR sensitizers, by correlating the results both to the structural characteristic of the molecule and to the dipping condition.

We are firmly convinced that this approach will make possible to find the optimal experimental conditions to achieve, within a good reproducibility, optimized performances, both in term of efficiency and long term stability.

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The effect of the central metal ion on photovoltaic performances of phthalocyanines used as sensitizers in DSSC

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The absorption properties of \Box -extended macrocycles such as porphyrins and phthalocyanines have been intensively applied to the light -harvesting process related to organic photovoltaics, with particular focus on polymer cells and Dye-Sensitized Solar Cells¹. In the last few years a large amount of new phthalocyanines have been synthesized and studied and amongst them an interesting sterically hindered *push-pull* structure, having a record efficiency value of 6.4%² has been prepared and published. Even if porphyrins have obtained higher values in terms of efficiency, having the most efficient ones recently shown an impressive efficiency value of 12%, thus comparable to that of N719^{3a,b}, the outstanding stability and high molar extinction coefficients (e> 10⁵) of phthalocyanines make them very attractive sensitizers with possible applications in Graetzel cells and justify the intensive study carried on these molecules.

It is well known that the metal centers of these macrocyclic compounds can affect their absorption peaks, their HOMO/LUMO energy values as well as their possible charge transfer properties in a DSSC device. Thus our goal was to investigate the performances of dyes possessing the same molecular structure having different central metal ions, in order to understand how their harvesting capabilities could be influenced by this kind of substitution. In particular we have chosen an unsymmetric tri-*ter*-butyl phthalocyanine bearing an ethynylbenzoic unit as anchoring group to the TiO₂, that have been synthesized and fully characterized by our research group some years ago as zinc complex⁴.

In the present contribution, the synthesis of different 9(10),16(17),23(24)-tri-*ter*-butyl-2-[acetynyl-(4-carboxy)phenyl]phthalocyaninato metal complexes and their optical, chemical and electrochemical characterizations will be presented. The related free-base phthalocyanine will also be analyzed. Theoretical calculations of both frontier molecular orbitals and simulated absorption spectra with the preliminary measurements of the related DSSCs, where obtained, will be also discussed.

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Far-IR Photoinduced Absortion in Organohalide Lead Perovskites

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The high photovoltaic energy conversion efficiency, exceeding $15\%^{1, 2}$, achieved by using organohalide lead perovskites (CH₃NH₃PbI_{3-x}Cl_x; x≥0) as active layer in solid state dye-like solar cells have attracted an increasing interest on these materials both in improving device performances and in understanding the reasons of their behaviour.

The large diffusion length for both electrons and holes observed in these materials³ are probably the base in understanding the high energy conversion efficiency of photovoltaic devices realized using organohalide lead perovskites as active materials. With this in mind it is important to understand which kind of charged quasiparticles are involved and how they interact.

The vibrational response of these systems instead can provide very useful information on their dynamics⁴. Moreover, the variation of this response when carriers are injected or photogenerated (IR photoinduced absorption - PIA) can also provide information on possible interaction of mobile carriers with the lattice.

Here we show that even at room temperature steady state PIA (exciting at 488 nm) is showing the bleaching of two IR modes and the appearance of a new one in the Far-IR indicating that photogenerated carriers are long lived and locally induce a deformation of the lattice changing the symmetry and relaxing the infrared absorption selection rules. This result suggests a strong electron phonon interaction in organohalide lead perovskites similar to what has been previously observed in high temperature superconducting perovskites⁵.

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Interfacial Engineering of P3HT/ZnO Hybrid Solar Cells by Phthalocyanines: a Joint Theoretical Experimental Investigation

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The present work[1] combines atomistic simulations and experimental investigations to study heterojunction interfaces of hybrid polymer solar cells, with the aim to better understand and precisely predict their photovoltaic properties. A state-of-the-art theoretical multiscale approach rooted on ab initio calculations[2], has been used to model an original, hybrid ternary system based on a P3HT/Zinc Phthalocyanine (ZnPc)/ZnO interface[3,4], in which a ZnPc interlayer is applied to improve the performance of the hybrid interface.

The theoretical findings have been then validated against the properties of concrete P3HT/ZnPc/ZnO planar heterojunction devices. Our theoretical predictions are in close agreement with the photovoltaic properties obtained in such a kind of P3HT/ZnPc/ZnO solar cells, indicating the strength of the present approach for modeling hybrid heterojunction interfaces. In detail, our jointly obtained theoretical and experimental results reveal that: (i) ZnPc molecules in direct contact with a ZnO surface insert new energy levels due to a strong ZnPc/ZnO coupling[3] (ii) electron injection from these new energy levels of ZnPc into ZnO is highly efficient, (iii) the ZnPc/ZnO coupling strongly influences the energy levels of the ZnO and P3HT leading to a reduction of the open circuit voltage, and (iv) charge carrier recombination at the P3HT/ZnO interface is reduced by the ZnPc interlayer. In practice, the intercalation of ZnPc leads to an increase in photocurrent as well as to an overall increase in power conversion of the planar hybrid heterojunction by 50%, thus stressing the importance of interfacial engineering in hybrid solar cells.

This work was developed as a collaboration between CNR-ISM Montelibretti (RM), CNR-IOM Cagliari, and CNRS-CINaM (Marseille,France) within the IIT-SEED Project POLYPHEMO funded by Italian Institute of Technology.

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A study on flavylium salts as bio-inspired sensitizers for dye-sensitized solar cells

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Here we present a computational and spectroscopic study on a family of cheap, non-toxic, environmentally friendly flavylium sensitizers. We followed a bio-inspired strategy and with the adequate structural modifications of the 2-phenyl-1-benzopyrylium core (flavylium) prepared quasi-natural biomimetic dyes. With this strategy we prepared a series of new anthocyanin analogues. Among these, in the 7-(N,N-diethylamino)-3',4'-dihydroxyflavylium (AD65),which is our best sensitizer, the diethylamine acts as an electron donor (D), the catechol moiety complexing with Ti(IV) in ring B behaves as an acceptor (A) and the benzopyran systems (rings A and C) constitute a π bridge defining a D- π -A structure similar to a "push and pull" sensitizer. More recently, with AD65 we obtained a solar conversion efficiency of 3.6% with an open circuit voltage of 0.4 V and a short-circuit current density of 16 mA/cm2. In order to improve the DSSC performances, part of our strategy involves extending the absorption range to the near-IR regime in order to attain good overlap with the solar emission spectrum and to produce large photocurrent responses. We prepared and assembled all the DSSC's components and fully characterized their photovoltaic performances.

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Transparent Conductive Oxides as Near-IR Plasmonic Materials for Energy Conversion

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Noble metals are conventionally used as plasmonic building blocks in the fields of telecommunications and energy conversion. Both localized surface plasmons in nanoparticles and surface plasmon polaritons (SPP) at metal/semiconductor interfaces are of interest for optoelectronic applications: the formers can be exploited in photovoltaic systems as amplifier antenna; the latters provide the opportunity of confining and propagating light over a long spatial range [1].

However, metals are plagued by large losses in the UV–vis and IR spectral ranges, arising from interband transitions and dissipative scattering events. As an alternative, heavily doped semiconductors, such as transparent conductive oxides (TCOs), can exhibit a small negative real permittivity and very small losses at the infrared and longer wavelengths [2].

Using first principles calculations, we investigate the origin of near-infrared plasmonic activity in Al-doped ZnO (AZO), one of the most promising indium-free TCO materials for optoelectronic and photovoltaic applications. Our results [3-4] predict realistic values for the plasma frequency and the free electron density as a function of the Al-doping, in agreement with recent experimental results. We further reveal the formation of SPPs at the AZO/ZnO interfaces indicating characteristic lengths that can be measured by experiments. These systems present tunable plasmonic activity in the near-IR range and in particular at wavelength also relevant for telecommunications $(1,5 \ \mu m)$ [3].

The direct comparison with standard plasmonic metals underlines the promising capabilities of TCOs as compact and low-loss plasmonic materials for energy conversion applications and telecommunications.

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Mesostructured TiO₂ films with ordered porous structure for photovoltaic devices

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Mesoporous materials with crystalline frameworks, high surface area and tunable pore size have received extensive research attention because of their potential applications in many fields, such as photocatalysis, electrochromism, energy storage and conversion.

On the basis of these considerations, highly porous titania films with a well-defined size and geometry of the cavity are promising candidates to improve the performance of dye-sensitized solar cells (DSSCs). Mesostructured titania films prepared by a soft template assisted route are characterized by huge surface area, few grain boundaries and uniform pore structure with excellent connectivity of mesopores. All these features are key aspects in the preparation of titania-based photoanodes, since they affect the efficiency of the photovoltaic devices. Ordered mesoporous titania films could also significantly improve the degree of dispersion of the adsorbed dye and increase the surface of dye/titania interface.

One of the most common routes for the production of mesoporous oxides with ordered mesostructure is the sol-gel synthesis in the presence of organic templates, such as block copolymers. These procedures offer many advantages, as low temperature, high scalability and low cost equipments.

We thus have prepared novel mesostructured titania films and exploited their versatility to improve the performance of titania-based solar cells.

Our recent findings have shown that bifunctional photoanodes with a double-scale morphology, which comprises a meso-ordered thin titania buffer layer and a main layer consisting of wellorganized clusters of nanocrystallities, allow to achieve as high energy conversion efficiency as 9.7%. By using hierarchical mesostructured photoanodes, the DSSC efficiency was improved by 50.0% with respect to devices based on commercial P25.

Highly ordered thin titania films, applied as an interfacial layer between the nanocrystalline main photoanode and the FTO electrode, suppress the back-transport reaction by blocking direct contact between the electrolyte and the transparent conductive oxide and provide excellent adhesion of the upper titania layer to the FTO.

The main layer consists of hierarchical structures prepared by soft template assisted route and composed of nanocrystallites that cluster in well-organized larger secondary particles, thereby functioning as light scatterers without sacrificing the internal surface area which is indispensable for a good dye-uptake and light harvesting efficiency.

Ordered mesoporous titania films have also shown promising performance in solid state devices.

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The real face of the methylammonium lead iodide perovskite coverage over a TiO₂ scaffold

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The largely debated but not still proven direct evidence of the formation of a thin film CH₃NH₃PbI₃ coverage on mesoporous scaffolds was here disclosed by a cross-correlation between different analytical techniques, namely angle resolved X-ray diffraction, Transmission Electron Microscopy, Scanning-TEM, Energy Dispersive X-ray and Electron Energy Loss Spectroscopy, using a sub nanometer e-beam probe. Fragments of the active material containing agglomerates of TiO₂ nanorods plus perovskite were isolated and studied in details at the nanoscale. In those regions the perovskite has a tetragonal lattice structure different to what found at the surface. By the local analyses, we demonstrated that perovskite thin layers uniformly enfold the TiO₂ surfaces even deeply infiltrating in the very sharps gaps (1-2nm) between adjacent TiO₂ nano-domains. It is now clear that perovskite and TiO₂ establish an intimate structural relationship, thus creating a prerequisite to assure a percolation path along the perovskite active material. The coverage can deteriorate leaving spheroidal pure Pb aggregates at the TiO₂ surface generating some misleading information in the literature.



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Engineering semiconductor nanostructures for photovoltaic applications

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Excitonic solar cells (XSCs)¹ are appealing candidates as alternative devices for solar energy conversion, being in principle low cost, rather environmental friendly and suitable for exploiting both diffuse light and the near infrared region of solar spectrum.

This lecture focuses on the design of semiconductor nanostructures to be applied as functional elements in photovoltaic devices: modulation of both composition and shape of nano- and micro-structured electrodes is key element to tailor the physico-chemical processes regulating charge dynamics and, ultimately, to boost the efficiency of XSCs, by favoring charge transport and collection, while reducing charge recombination.

In particular, dye- and quantum dot- sensitized solar cells (DSSCs and QDSSCs, respectively) will be considered. Discussion will be focused on the:

- 1. preparation of hybrid organic-inorganic composites (multiwall carbon nanotubes/graphene sheets and TiO₂ nanoparticles) to be applied as photoanodes in DSSCs to boost the device functional performances. Results indicate that integration of multiwall carbon nanotubes (or graphene flakes) below the percolation threshold is key for enhancing the short circuit current while preserving good open circuit photovoltage values by a proper band alignment between the hybrid photoanode and the light harvester;²
- 2. fabrication of hierarchically assembled Cu₂S structures to be integrated as cathode in QDSSCs, as an example of effective coupling of material design simplicity with material enhanced functionality and reproducibility, which is currently an issue in the fields of QDSSCs. Results indicate how the proper material design and device engineering can lead towards functional performance enhancement and experimental reproducibility.^{3,4}

Strategies devoted to improve light managing, charge generation and collection and catalytic performances for electrolyte regeneration will be as well highlighted, together with the actual possibility to exploit simple, cheap and low environmental impact techniques for advanced material preparation.

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Inside Nature Materials - an editor's view

Luigi Martiradonna

Nature Materials, The Macmillan Building, 4 Crinan Street, N1 9XW London (UK)

Nature Materials offers authors high visibility to their work. A team of full-time, professional editors selects and commissions articles that have the best chances to appeal to the journal's broad audience. In this talk I will convey the editor's perspective on the life of a manuscript after submission to Nature Materials, and comment on the efforts aiming to improve the transparency of manuscripts reporting advances in photovoltaic applications.

POSTERS

Deep investigation of degradation mechanisms affecting long-term stability in reverse biased Dye Sensitized Solar Cells

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Dye-sensitized solar cells (DSCs) technology has attracted great attention as a third generation photovoltaic, due to its low solar energy conversion cost and high performances. However, the high stability and the ageing predictability are not-fully reached requirements for its industrial development yet. As a matter of fact, several degradation mechanisms affect chemical constituents of a DSC during the real working conditions when the cell in a module is forced to work under reverse bias (RB) regime, induced by shadowing phenomena.

It is possible to reproduce RB regime by an accelerating procedure that consists in applying a fixed current of about 120 mA (three times the short circuit current at 1 Sun solar irradiation) to the cell.¹

The prolonged stress causes visible degradations that involves both electrolytic solution and the sensitizer.

Largely before complete device's breakdown, consisting in a turbulent bubbling of electrolyte solution causing electrolyte leakage from active area and strong color heterogeneity on photo-electrode, we detected polyiodides species in electrolyte solution by micro-Raman spectroscopy technique.

Furthermore fluorescence measurements reveal a marked emission affected by Red Edge Effect (REE) that has been attributed to the formation of various associated structures among 1-methyl-3-propylimidazolium iodide (PMII) ions in electrolyte solution.

The previous electrolyte modifications have a huge impact on the device electrochemical working principle and take the form of a gradual increase of the anodic operating voltage (V_{RB}), while the diffusion-limited current (I_{lim}) is strongly decreased due to the I_3^- depletion in electrolyte solution.¹ Since diffusion dynamic of electrolyte ions is strongly affected, dye molecules are retained in a prolonged oxidation state that eventually favors dye irreversible structural changes, clearly visible in strong color heterogeneity on N719 sensitized photo-electrode.

As a consequence of the severe degradation of cell components, electrolyte bubbling phenomena occur and, as a consequence, the break of the sealing, the leakage of electrolyte solution and the breakdown of the device.

Raman spectroscopy on a completely degraded solar cell clarified that the apparent N719 dye bleaching in particular zones of the cell active area, can be reasonably attributed to the irreversible structural changes (involving SCN⁻ ligand) that affect dye molecule in some zones of PE which are not in contact with electrolyte solution, during the turbulent final stages of RB stress test. ^{2,3}

The deep comprehension of degradation mechanisms is surly the key factor to improve the long-term stability of the promising DSC technology and makes the industrialization possible.

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Benzodithiophene-Based Push-Pull Organic Dyes for DSSC: Photophysical, Electrochemical and Photovoltaic Properties

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The most efficient metal-free dyes for DSSC are characterized by a push-pull structure in which an electron-donor group is connected to an electron-acceptor one through a wide \Box -conjugated system. A number of aromatic and heteroaromatic conjugated molecules have been investigated as \Box -spacers, and dyes comprising thiophene rings have already shown remarkable efficiencies when employed in DSSC. We have already reported¹ some preliminary results about the synthesis, spectro-electrochemical characterization and cell efficiency of two new organic dyes (CR29 and CR52) containing, as π -conjugated spacer, linear (BDT₁) and angular (BDT) benzodithiophene structure. (Figure 1)





BDT₁ system, because of its better conjugation, proved to be the more efficient π -bridge and on this basis we extended the design of BDT₁ based push-pull dyes, with the aim of establishing a structure/performance correlation. A series of molecules, derived from the parent CR29 dye, in which a bulky alkyl chain is present on triarylamine or benzodithiophene unit has been synthesized. The novel chromophores have been the object of a detailed molecular electrochemical study, focusing on the electron transfer properties as a function of the conjugation efficiency of the spacer system and of the substituent effects. The new dyes have been tested in liquid DSSC cells, investigating the dependence of the photovoltaic properties of devices upon: i) different types of anatase TiO₂ photoanodes ii) electrolyte solution concentration and composition iii) the amount of chenodeoxycholic acid (CDCA) as a de-aggregating co-adsorbent agent.

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Tuning the optical properties of MoS₂ single layer via organic functionalization.

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Recently two-dimensional layered materials based on transition metal dichalcogenides (TMD) have received a large amount of attention because of their peculiar and versatile physical properties [1]. In particular mono and few-layered TMDs are direct-gap semiconductors whose band gap energy, as well as carrier type (n- or p-) varies depending on the composition, structure and dimensionality of the system. In particular MoS₂ has been proposed as active absorbing layer in photovoltaic application due to its efficient absorption in the visible energy range [2] but also as photocatalyst for hydrogen evolution reaction [1]. The efficiency of MoS_2 in this kind of applications strongly depends on the ability of this material to absorb part of the visible spectra but also on the spatial localization of the electron/hole pair upon excitation. Moreover it would be important to be able to tune the conductivity of the MoS₂ monolayer (n- vs. p-) by accurately modifying its structure [3].

Here we present theoretical predictions of the electronic and optical properties of MoS_2 modified with different organic molecules, namely thiophenol, 4-nitrothiopheniol and 4-aminothiophenol. The nitro group and the amino group are known to function as electron attractive and electron donating groups respectively; as such, they are expected to function as p-type and n-type dopant respectively. In our work, the equilibrium structures of the hybrid $MoS_2/organic$ systems were obtained by means of *ab initio* density functional theory simulations, while absorption spectra were calculated employing the GW-Bethe Salpeter method. The proposed molecules are found to chemically bind to the MoS_2 monolayer through their sulfur atom and strongly modify the electronic structure of the monolayer. Our results show that the proposed molecules are able to effectively tune the absorption spectra of the MoS_2 monolayer and modify the spatial localization of the exciton.

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1D randomly rough substrate for light-trapping: Scattering properties

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Thin-film technologies may decrease the cost and reduce the bulk losses of a solar cell (SC). Yet, an enhancement of absorption by light-trapping is necessary for high efficiency. In this work, we investigate, both experimentally and theoretically, scattering properties of one-dimensional (1D) randomly rough substrates that provide strong and broad-band absorption enhancement of light in SC [1].

The sample is prepared recurring to a self-organized approach based on defocused ion beam sputtering. A low energy Ar+ beam impinges at grazing incidence angle on the surface of a polycrystalline gold film, which develops a nanoscale rippled pattern oriented along the beam direction. Metallic ripples form an array of disconnected nanowires which act as a sacrificial stencil mask for patterning the underlying glass substrate. The result of this process is the presence of 1D nano-ridges on glass surfaces [1]. The pattern is realized with a gradient in the roughness on parallel direction to ion flux. So we can investigate the angular resolved scattering (ARS) in relation to root-mean square (RMS) of peak height, a statistical parameter which describes the roughness.

In optical experiments we shine normally with unpolarized light on the substrate and collect the light scattered by the rough texture at various angles (Fig.1). Measurements are shown in Fig.2 as normalized intensity of scattered light vs collection angle. Interestingly, we observe that in the long-wavelength range the ARS increases with increasing the RMS: Zone 1 is almost flat, Zone 2 has a RMS=150nm and Zone 3 has RMS=100nm.



For Zone 2, the ARS in the long-wavelength range is broader than the cosine distribution corresponding to a Lambertian scatterer [2]. For Zone 3, that is well fitted by a Gaussian distribution of heights, we have compared the experimental results with the rigorous optical simulations of a 1D Gaussian roughness, described by the statistical parameters corresponding to the measured substrates [3]. The comparison gives a very good agreement between the experiment and theory, validating our computational model, and allows us to calculate the ARS of the

light transmitted into the silicon active layer – a quantity which is not accessible experimentally. Our final goal is to find the best statistical parameters of the scattering 1D rough glass/silicon interface to obtain a current enhancement in conformally grown thin-film SCs, similarly to that already observed in preliminary experiments on amorphous Si.

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Luminescent solar concentrators for building-integrated photovoltaics

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Luminescent solar concentrators (LSCs) are photovoltaic devices consisting of a dielectric layer (usually polymethyl methacrylate, PMMA) doped with luminescent dyes, which absorb a portion of the solar spectrum and re-emit light at longer wavelengths. Light is guided by total internal reflection within the slab and is collected by photovoltaic (PV) cells that are placed at the slab edges. The concept of LSC is having a large area of low-cost organic material, while the required area of high-efficiency solar cells is determined by the slab edges and is reduced by a concentration factor which increases with the system size. Moreover, LSCs lend themselves to the realization of semitransparent PV devices that can be suited for building integration.

In this work we report on the realization, characterization, and theoretical study of LSCs containing various fluorescent dyes developed at Istituto ENI Donegani. Such dyes allow to harvest light in different regions of the solar spectrum, and to tailor chromatic effects of the final PV device. Optimal dye concentrations are determined by means of a ray-tracing Monte Carlo code. In view of upscaling, optical losses in the considered LSCs are characterized by means of absorption and variable excitation spot experiments. Experimental results are in very good agreement with simulations.

We introduce a new concept of *cascade luminescent solar concentrator* (*c-LSC*) [1]. This consists of a primary LSC, typically of square shape, which is surrounded by secondary LSCs that are placed at the edges, in optical contact with the primary LSC. Light is then collected by high-efficiency solar cells places at the corners of the secondary LSC. In a c-LSC, the solar cell area is independent of the area of the concentrator – thus the concentration factor can be much higher than in a normal, single LSC (s-LSC). The ideal situation for a c-LSC is when the absorption spectrum of the secondary LSC fully overlaps with the emission spectrum of the primary LSC. In order to provide a proof of concept, we fabricate and characterize a prototype using diotiophenebenzothiadiazole (DTB) and Lumogen F305red dyes, for which the spectral overlap is sub-optimal. Preliminary experimental results are in good agreement with theory and demonstrate the potential of the concept.

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Low temperature synthesis of mesoporous titania films with ordered porous structure and high surface area for flexible solar cells

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The basic design principle for solar cells is to increase the optical absorption of the active layer and/or reduce the electron loss during transport. For dye-sensitized solar cells (DSSCs) it is well-accepted that a superior photoanode requires high surface area for a large amount of dye molecule loading and an optimal morphological engineering for light harvesting and fast electron transport. Ordered mesoporous TiO_2 thin films have attracted great interest as photoelectrodes for DSSCs due to their high surface area and crystalline frameworks with uniform pore structure and excellent connectivity of mesopores.

We have recently demonstrated that the use of highly porous mesostructured titania films greatly enhance the dye adsorption, improving the light harvesting and power conversion efficiency of DSSC devices. The synthesis of ordered mesoporous structure is usually carried out by the sol-gel procedure using triblock copolymers as soft templates, then thermal treatments at 350°C are necessary in order to remove the template and to gain a crystalline anatase structure. At the present, the development of highly efficient dye-sensitized solar cells obtained by using low

temperature processes is still an important and attractive challenge with the aim to lower thermal balance and cost for their production. Low temperature routes also enable the realization of flexible solar cells onto polyethylene terephthalate (PET) - based substrates thus opening the way to a wide range of applications.

On the basis of these findings, a low temperature method for the preparation of high surface area and mesostructured titana films onto conductive glass and PET has been developed. By using synthesis carried out at temperature of 100-150 °C, the formation of crystalline anatase was attained. The main advantages are the preservation of the mesoporous structure with an increased surface area and the possibility to prepare mesostructured titania films onto flexible substrates.

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Bis(triisopropylsilylethnyl) Pentacene/Au(111) Interface: Coupling, Molecular Orientation and Thermal Stability

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The assembly and the orientation of functionalized pentacene at the interface with inorganics strongly influence both the electric contact and the charge transport in organic electronic devices. In bis(triisopropylsilylethnyl)pentacene (TIPS-Pc) the TIPS functional groups not only improve the solubility in common organic solvents, but also features good transport properties arising from the "brick-wall" face-to-face arrangement of the molecular planes, that increases the intermolecular interactions with respect to the edge-to-face "herringbone" stacking of pentacene.

In order to understand and control the assembling of TIPS-Pc on the Au(111) surface, we have combined electronic spectroscopies and theoretical modeling to investigate the properties TIPS-Pc/Au(111) interface as a function of the molecular coverage, to compare the molecular state in the gas- and in the adsorbed-phase and to determine the thermal stability of TIPS-Pc in contact with gold.

Our results show that in the free molecule only the acene atoms directly bonded to the ligands are affected by the functionalization. Adsorption on Au(111) leads to a weak coupling which causes only modest binding energy shifts in the TIPS-Pc and substrate core level spectra. In the first monolayer the acene plane form an angle of $33^{\circ} \pm 2^{\circ}$ with the Au(111) surface at variance with the vertical geometry reported for thicker solution-processed or evaporated films, whereas the presence of configurational disorder was observed in the multilayer. The thermal annealing of the TIPS-Pc/Au(111) interface reveals the ligand desorption at ~ 470 K, which leaves the backbone of the decomposed molecule flat-lying on the metal surface as in the case of the unmodified pentacene. The weak interaction with the metal substrate causes the molecular dissociation to occur 60 K above the thermal decomposition taking place in thick drop-cast films.

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Novel hybrids of W-Ti polyoxometallates and polyalcohols for optical and energy storage applications.

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Hybrids including organic and metallic species can display new interesting light and redox induced functionalities that can give rise to photoinduced energy- and electron-transfer processes. These properties can be potentially exploited for very different purposes from photoinduced non-linear optic applications to solar energy harvesting and storage to photocatalysis¹. Indeed, hybrids of titanium oxide hydrates and polyalcohols show intense photochromic response from colourless to blue^{2,3} over irradiation to UV-near visible light. This phenomenon results from a photoinduced redox reaction involving the two components of the hybrid which leads to the reduction of the metal centers and consequently to charge transfer mechanisms among the reduced metals. The colouration can be fully reversed over exposure to air. In this work we enhanced the photochromic response of such hybrids by introducing tungsten in the structure of titanium oxide hydrates. Molecular hybrids systems based on titanium-tungsten-polyoxometallates and polyalcohols thus displayed faster, more intense and stable photochromic response respect to the previous set of hybrids. We observed that the enhancement of the photochromic behaviour of the hybrid systems increased with the content of tungsten in mixed metal oxide hydrates structures (up to 100 folds higher than in absence of W) and that this metals act as charge depositories of the hybrids. Our work thus highlighted that the photochromism of these novel materials based on titanium oxide hydrates and polyalcohols can be exploited not only for optical applications but also for solar energy harvesting and storage purposes.

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Titanium oxide hydrates/ PVAl hybrids based photonic structures for lightmanagement in organic optoelectronic devices

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The Organic Optoelectronics field increasingly focuses on the development of new materials that allow enhanced light management (through use of, e.g., input-/output-coupling structures and waveguides) and, thus, the performance of devices such as organic light-emitting diodes, organic photovoltaic cells, etc.... However, so far, versatile and easy-to-process materials are still lacking that would allow straight-forward manufacturing of such light-management architectures and/or ready integration of them into organic-based optoelectronic devices. In order to address this issue, we have developed solution-processable hybrid materials based on titanium oxide hydrates and polymer matrices such as poly(vinylalcohol) that display refractive indices *n* varying between 1.52 and 2.1 (at 550 nm), are highly transparent in the visible and near infrared regime and allow manufacturing of complex architectures like one- and two-dimensional photonic crystals through simple and inexpensive techniques such as solution-molding. Furthermore, it is possible to widen the spectrum of optoelectronic properties of these hybrids to tailor them for specific applications by simply modifying their formulation through addition of different metals chosen with respect to their chemistry, dimensions, and optical and electronic properties of their oxides. As a proof of concept we analysed the effect of the introduction of Zr, Hf, W, Ga, In, Tl and Eu selected with the aim to improve the refractive index window of the hybrids and/or impart them an enhanced conductivity or emissivity. The optical properties of the obtained structures were then analysed and discussed in light of potential applications.

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Di-branched Thiophene-Based Phenothiazines for Dye Sensitized Solar Cells and Solar Hydrogen Production

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Till now most of the renewable sources focused on the production of electric energy, but the world demand is composed of both electricity and fuels. Thus, in recent years hydrogen production from renewable sources has attracted the attention of many research groups. Splitting of water molecules is energy demanding and solar radiation could provide such request. Inspired by DSSC technology, an analogous mechanism can be thought for water splitting. In our research we focused the attention on the reduction semi-reaction from water to hydrogen, using a sacrificial electron donor. In particular we were interested in developing new classes of organic dyes as photosensitizers for dye-sensitized photocatalytic production of hydrogen with Pt-TiO₂ as a multielectron catalyst.

We have recently introduced a new design approach for metal-free sensitizers based on a multibranched geometry, for improved light harvesting and enhanced stability compared to the conventional linear D- π -A sensitizers. Here we present the effect of different conjugated π -spacers in hydrogen production and DSSC performances. We tested molecules with a D-(π -A)₂ structure where D is a phenothiazine donor core, A is the acceptor-anchoring cyano-acrylic group, and π varies in different thiophene derivatives. Optical characterization highlighted the differences in dye properties, such as higher molar extinction coefficient and longer absorption maximum while increasing the length of the conjugated path.



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New hybrid photoconverters based on organic dyes and photosynthetic proteins

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Covalent binding properly tailored organic dyes to photosynthetic proteins extracted from plants or bacteria represents a powerful approach to develop new hybrid biomimetic photoconverters capable of exploiting solar energy to generate photocurrents or to drive chemical reactions. These systems are appealing for applications in various fields, including photocatalysis and photovoltaics.

We have developed the first bio-hybrid photoconverter in which a tailored organic aryleneethynylene dye (AE) has been covalently anchored to selected amino-acids of the photosynthetic protein (the reaction center RC) isolated from the purple *Rhodobacter sphaeroides* bacterium.[1] In particular, we have demonstrated that AE effectively acts as light harvesting antenna and transfers energy to RC (Figure 1), enhancing its activity at a single excitation wavelength which the native biological system does not efficiently absorb.



Figure 1

More recently, we have designed and synthesized new molecular fluorophores having photophysical properties that fulfill better than AE the requirement to act as antennas for RC. In particular, the new assembly can be excited in the whole visible range by white light.

Synthesis and properties of the bio-hybrid photoconverters will be described in the communication.

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Low Environmental Impact Synthesis of a Highly Performing Organic Sensitizer *via* Direct Arylation Reactions

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The presentation deals with the low environmental impact synthesis of a highly performing \Box -extended organic sensitizer (G3) for applications in dye-sensitized solar cells. The material was endowed with a D- π -A structure using the simplest available units for the construction of the electron-donor group (a triarylamine), the \Box -conjugated spacer (the dithienyl-benzothiadiazole chromophore) and the acceptor/anchoring region (phenyl cyano-acrylic acid).



In order to decrease the environmental impact associated to the preparation of the dye, the *green metrics* of the traditional synthetic approach based on cross-coupling reactions using organometallic compounds were compared with those of a synthetic route exclusively based on C–H bond activation reactions, observing a great improvement in the case of the latter method.



The sensitizer G3 was fully characterized by UV-Vis, cyclic voltammetry, DFT calculations and a remarkable power conversion efficiency of 8.64% was obtained in DSSC applications. The described results clearly indicate that, in view of the potential scale-up of the dye production, the molecular engineering aimed at searching highly performing organic sensitizers can be associated to the control of the environmental impact related to their synthesis by the choice of a judicious synthetic approach.

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Synthesis of conjugated electrochromic polymers based on anthraquinone units

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9,10-Anthraquinone-based compounds have recently attracted considerable interest for their use in medicinal chemistry, photovoltaic technology, bulk chemical industry.

Recently, organic polymers with the electron-donor polythiophene skeleton bearing electron acceptor anthraquinone side groups have been studied as potential electrochromic materials.¹

Here we report the synthesis and preliminary characterization of new organic polymers with the electroactive anthraquinone moieties in the main chain alternated to dithiophene or carbazole units (Figure 1). These polymers have been obtained by palladium catalyzed cross-coupling reaction of 2,6-diiodo-1,5-bis(octyloxy)-9,10-anthraquinone² with commercially available organometallic reagents.

Electrochromism of the resulting materials has been investigated and preliminary results will be reported in the communication.



Figure 1

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Chemical functionalization of melanin-like materials

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Melanins are a class of dark macromolecules found throughout in nature, mainly with photoprotective and pigmentary functions, but their presence in tissues not exposed to light suggests that they may play some other roles and functions.¹

Recently, synthetic melanins have been suggested as bio-inspired materials for applications in organic bio-electronics, due to their peculiar hybrid electronic-protonic conducibility.²

In this work we report some strategies for the chemical functionalization of melanin-like materials in order to open the possibility of tuning their chemical and physical properties, and to enable processability from aqueous solutions. In particular, we focused on two classes of synthetic melanins: polydopamines and poly-dihydroxyindoles.

Polydopamines are bio-inspired melanin-like materials that can be deposited as homogeneous and conformal thin films from a water solution of precursors, and whose electrical properties can be tuned by copolymerization with suitable co-monomers.³

Poly-dihydroxyindoles, by contrast, are synthetic melanins deriving from the oxidation in biomimetic conditions of the 5,6-dihydroxyindoles (DHIs), which can be functionalized at the N-position thus producing functionalized melanins. By the latter approach, we have synthesized a water-soluble melanin from DHIs functionalized with a triethyleneglycol chain. Furthermore we proved the filmability of the material, and performed an electrical characterization of the film that revealed an electrolyte-like behaviour.

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Controlling the functionalization of carbon nanostructures for energy related materials

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Synthetic procedures that have been developed to functionalize carbon nanostructures (CNSs) such as nanotubes (CNTs) and grapheme nanoplatelets (GNPs) may require long reaction times and harsh conditions. Moreover, unlike common molecules, resulting products are hardly associated to a specific structure and may be rather described as a distribution of derivatives. In this context we have studied the continuous flow processing of carbon nanostructures with the aim not only to reduce reaction times but also to tune the properties of the functionalized carbon materials. We demonstrated the generation of reactive azomethine ylides through different routes. A standardized characterization protocol, which merges UV/Vis/NIR, Raman, DLS and TGA, was employed to compare the products. Our methodology leads to derivatives with similar functionalisation degree (FD) of those reacted in a flask but with reaction times dramatically reduced compared to batch conditions [1,2] and a productivity almost two orders of magnitude higher. Interestingly, the solubility distribution of the products depends on the route that one selects to generate the ylide.[4] This finding could be of help to design synthetic strategies for specific applications that benefit either from a small fraction of product with very high solubility or from a larger amount with an average FD. The flow methodology was also extended to the fast and effective addition of diazonium salts to CNTs and also to the functionalization of GNPs. Besides reducing processing time, the flow approach allows to control the degree of CNTs functionalisation, leading to derivatives with enhanced solubility that retain the electronic properties of pristine tubes and can be used for organic electronics or photovoltaic applications [3].

In this perspective, we observed how an increase of FD affects the electronic communication of CNSs with a conjugated polymer (P3HT).[4] Our findings show that this is due not only to an increased density of defects, but probably also by the formation of multilayered organic structures that shield the carbon lattice [5].

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Electronic and photovoltaic properties of the CH₃NH₃PbI₃ perovskite from a Car-Parrinello Molecular Dynamics perspective

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In the recent years, methylammonium lead-halide perovskites based solar cells have shown an impressive improvement in their performances [1] but, in spite of these results, many open questions about the basics of these materials remain to be addressed. Peculiarity of these hybrid perovskites is the presence of methylammonium cations (MA), having a permanent dipole, that are free to rotate inside the cubo-octahedral PbI cage. The orientation of the MA cations within the perovskite is thus expected to play an important role on the dielectric properties of this class of materials [2]. In this regard, ferroelectricity has been recently observed in the tetragonal phase of MAPbI₃ [3].

We present here the results of Car-Parrinello molecular dynamic simulations, aimed to unveil the atomic structure of this class of material from a dynamical perspective, supported by static DFT calculations. Considering here two kind of orientational configurations, i) with a net alignment of the MA cations (which are likely to be ferroelectric) and ii) without a net alignment of the cations (which are likely to be antiferroelectric) we show that the anti-ferroelectric structure is less stable, but that the transition towards more stable structures is slow and much longer than the timescale of our dynamics (>> ps).

Moreover, we show that peculiar electronic effects, like the presence and the magnitude of the Rashba splitting and the presence of band bending on the material surface, are also affected by the cation orientation.

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Croconaine dyes: a promising class of IR sensitizers

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Dyes that absorb in the near-infrared region (NIR) of the spectrum have gained increasing attention in the past few years,¹ especially because of their optoelectronic² and biomedical³ application. One synthetic strategy commonly used is to increase the extent of π -conjugation of well-known dyes. This approach may cause negative effect on the chemical and/or photochemical stability. The donor-acceptor-donor concept was introduced to solve these problems and utilized for the synthesis of long-wavelength absorbing dyes.

Croconaines are a class of dyes, closely related to squaraines, still not so cited in the scientific literature, that seems to be very attractive in relation to their properties as NIR sensitizer, although they have been used for different purposes. Furthermore, their synthetic protocols are easily accessible, they are chemically stable and have high molar extinction coefficients.

The pentatomic ring of the croconaines has higher electron acceptor efficiency, if compared with the corresponding squaraines, showing a red-shift of almost 100-120nm.⁴

We report the synthesis of a series of croconaines derivatives that will be evaluated as sensitizers in DSSC photovoltaic cells.



Figure 1. Schematic representation of a Croconaine dye where Donor groups are Aromatic or Heteroaromatic groups.

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Langmuir-Schaefer Films of Aligned Carbon Nanotubes Blended with Conjugate Polymers and their Photoelectrochemical Response

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Alkoxy-substituted poly(arylene thiophene)s are used to suspend single-walled carbon nanotubes (SWCNT) in (E)-1,2-dichloroethene (DCE). The functionalization of SWCNTs, with a phenylene-thiophene polymer (POPT) (1) and a low band-gap polymer alternating dialkoxyphenylene-bisthiophene units with benzo[c][2,1,3]thiadiazole monomeric units (2), is based on non covalent interactions. The suspended blends were transferred on ITO substrates by Langmuir-Schaefer deposition method, resulting in a film with high percentage of aligned nanotubes. Subsequent photoelectrochemical characterization of thin films showed the benefit of the SWCNT alignment for photoconversion efficiency(3).

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Donor-acceptor 1,2-hemisquarimines

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In this presentation we report the synthesis of a new class of robust squaraine dyes, colloquially named 1,2-hemisquarimines (1,2-HSQiMs) through the microwave-assisted condensation of aniline derivatives with the 1,2-squaraine core. In CH₃CN, 1,2-HSQiMs show a broad absorption bond with



band with

a high extinction coefficient and a maximum at around 530 nm, and an emission band centered at about 574 nm that are pH-dependent. Encapsulation of the chromophore into a cucurbit[7]uril host revealed fluorescence enhancement and increased photostability in water. The redox characteristics of 1,2-HSQiMs indicate that charge injection into TiO_2 is possible, opening promising perspectives to their use as photosensitizers for solar energy conversion.

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Tuning of Down-Converted Emission in Oligoacenes Co-Crystals for Thin Film Luminescent Solar Concentrators

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In the past few decades, organic single crystals based on π -conjugated molecules have been extensively studied and employed in the field of optoelectronic materials.⁵ Indeed, their definite structures provide a model to investigate relationships between molecular stacking modes and optoelectronic performances.

Acene based dyes are known to have a significant fluorescence quantum efficiency in solution.² This efficiency is partly quenched when going to the solid state, because of aggregation effects. Oppositely, in order to obtain well performing optoelectronic devices it would be necessary to retain good efficiencies in the solid state. Recently, organic molecular host/guest co-crystals based on oligoacene materials have been shown to promote a very efficient host-to-guest energy transfer at very low concentrations of guest species due to the head-to-tail transition dipole alignment taking place upon crystal formation.³ Due to the very high *Förster-type resonance energy transfer* (FRET) of these systems,² highly fluorescent films can be obtained by doping a polymer solution with such molecular co-crystals and by using conventional wet processing techniques to deposit the luminescent doped films on appropriate substrates.

In addition to retaining a significant luminescence efficiency, these systems offer also the possibility of tailoring the emission of the down-converted radiation. This makes them suitable candidates as active components in *organic luminescent solar concentrators* (OLSC), which currently represent a promising technology to reduce manufacturing and installation costs of conventional photovoltaic modules.

In this frame, we have recently reported the preparation of fluorescent films based on PMMA doped with anthracene/tetracene (Ac/Tc) host/guest co-crystals and on their use as OLSCs for mc-Si solar cells.⁴ The fluorescent polymeric films were obtained by spin-coating a solution of PMMA containing Ac and Tc on a glass substrate. By varying processing conditions different co-crystal morphologies could be obtained that were found to influence the performance of the corresponding OLSC devices. An absolute efficiency η_{OLSC} as high as 2.50% was found for our best OLSC device, with an optical efficiency η_{opt} of 23.72% and a concentration factor *C* of 0.83%. Details on morphologies and optical properties of the films will be given as well as the OLSC preparation and characterization.

Finally, tuning of the emission wavelength can be achieved by changing the guest molecule. Results on tetracene/pentacene (Tc/Pc) co-crystals will be reported showing that good fluorescence quantum yields and efficient FRET can be obtained together with a longer emission wavelength which better matches the mc-Si band gap.

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Functionalization of nanostructured biosilica from *Thalassiosira weissflogii* diatom with luminescent organic molecules

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Catalysis, separation and sensing extensively exploit mesoporous silica adsorption properties. Micro- and nano-texturing are known to be remarkably useful for photonic and biological applications. Diatoms are a prolific class of single cell photosynthetic algae with microscopic 3-dimensional silica shells, called "frustules", which exhibit highly porous, nanopatterned surfaces attractive for many applications including photonics [1], molecular separation [2] and biosensing [3]. Frustules are produced by diatoms biosilicification processes. These are polymorphic silica structures, with an highly hierarchic and symmetric organization of the morphological features, and their biosynthesis is based on silicatein-silaffin proteins interactions with silica-derived compounds, and on a combination of bioorganic scaffolds which exhibit positive charges and a highly efficient way of nanoguided-precipitation[1].

Interfacing diatom frustules with biological or chemical moieties, *e.g.* DNA, enzymes, proteins, antibodies, optically active dyes and magnetic nanoparticles, can be achieved through tailored chemical functionalization [4].

We have used biosilica from *Thalassiosira weissflogii*, a pelagic centric diatom from Oceans, for building luminescent bio-hybrids (fig. 1) useful as fluorescent micro/nano- structures and photonic platforms.

We developed chemical protocols for the modification of the outer surface of *Thalassiosira weissfloggii* diatom frustules with organic dyes *via* the APTES-method. We have also demonstrated the possibility to produce nano-structured micro-systems consisting of organic photo-active molecules (heteroaromatic conjugated molecules) covalently grafted on diatom frustules by feeding living diatoms with triethoxysilane-modified dyes.



Fig. 1. Top: red-emitting benzothiadiazole-based molecule addresses frustules after extraction from living diatoms; Bottom: blue-emitting phenyleneethynylene based molecule for in vivo labeling of diatoms (red spots are chloroplasts mottles).

We started with the synthesis of two different light emitting conjugated compounds which are red- and blue-emitting molecules. These were obtained *via* synthetic protocols based on cross-coupling reactions *i.e.* Stille, Suzuki-Miyaura and Sonogashira reactions. The functionalization of the biosilica with the light emitting molecules was performed *via* the amide coupling reactions. We finally studied the chemical addressing of fluorescent molecules in the biosilica by a convenient *in vivo* derivatization protocol. The resulting luminescent micro/nano- structures have been investigated with fluorescence microscopy.

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Charge Extraction Layer for High Efficiency, Low-Temperature and Hysteresis-less Organo Lead Halide Perovskite Solar Cells

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Abstract

The recent and fast evolving interest in Perovskite-based solar cells has led to a development of several architecture and new design of the devices with impressive results.

On one side, the standard architecture based DSSC device using TiO_2 as electron acceptor layer and Spiro-OMeTAD as hole transport material has reported record efficiency high as 19.3%^[1]. Anyway this structure, beyond the high PCE reported, shows several problems and strong conditions in the devices realization that aren't yet solved; firstly the requirements of high temperature treatments and the doping process of Spiro-OMeTAD in air which took overnight exposure of the samples exposing to moisture degradation, secondly the presence of a strong hysteresis in the evaluation of the conversion efficiency in these devices put a foggy curtain on the real success of this architecture.

On the other hand several efforts have been done in order to solve the problems of the standard architecture, using new interlayer processable at low temperature that doesn't required slow doping processes. In this sense several work came out leading to an inverted structure of Perovskite solar cell which involved a bottom layer of PEDOT:PSS as hole extracting layer and PCBM as electron acceptor material^[2].

In this work we present a deep investigation on different materials can be used as charge extraction layer both for holes and electrons.

In detail, we optimized the inverted design of perovskite solar cells using interlayer material with specific characteristic as solution processability, room temperature treatments and improved stability. As result we obtained Power Conversion Efficiency more than 12% with high reproducibility of devices and without hysteresis effects in the evaluation of the PCE even changing the scan direction and the acquisition time.

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Excitons versus Free Charges: a Photophysical Picture of Organo-lead Tri-Halide Perovskites

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Very recently a generation of mixed organic-inorganic halide perovskites materials has emerged as a promising solution for photovoltaics. In the last two years perovskite based solar cells (PSC) have been characterized by a tremendous development achieving impressive power conversion efficiencies up to 15.7%. Interestingly it has been demonstrated that organic-inorganic halide perovskite can work efficiently in a variety of device architectures going from a dye sensitized concept, in which the perovskite crystals replace the dye on the TiO_2 mesoporous scaffold, to a meso-superstructured device architecture in which the TiO_2 is replaced by an Al_2O_3 mesoporous scaffold, proving that the perovskite crystals can also sustain charge transport. As a further evolution thin film architectures have been particularly successful demonstrating performances comparable to traditional inorganic thin-film solar cells. The variety of configurations in which they have been used along with the high performances demonstrated, cast the doubt on the fundamental physics governing the photovoltaic mechanism, in particular regarding the nature of the elementary photo-excitations, i.e. whether free charges or bound excitons are generated and their dynamics with a special attention to the electron transfer processes.

In this framework we address the photophysical properties of the $CH_3NH_3PbI_{3-x}Cl_x$. As a first step we focused on the optical properties of the perovskite deposited on bare glass. By temperature dependent absorption measurements we estimated the exciton binding energy to be about 55 meV. Using this value we model the thermal ionization processes using Saha equation leading to an evaluation of the branching ratio between free carriers and excitons at thermal equilibrium finding that at equilibrium there is a predominant fraction of free charges under photovoltaic operating regime.

However due to the critical role of structural interactions of the organic/inorganic components, different crystallization/deposition methodologies can lead to crystals with identical nominal chemical composition but with different macroscopic opto-electronic properties, for this reason we also focus on the investigation of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite thin films crystallized in situ on substrates of different natures (e.g. porosity, wettability) and we correlate their optical (i.e. UV-Vis absorption and photoluminescence) and structural properties.

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Crystallization of semiconducting:insulating polymer blends

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Organic electronic devices have attracted considerable interest over the last decade as they promise to provide an alternative to conventional, inorganic electronics platforms. There has been a rapid development in the area, and the drastic increase in device performance over the last few years has been driving these organic electronic technologies towards commercialization. Numerous advantages arise from the employment of polymeric materials and the possibility of combining the

commodity plastic and semiconductor industry to produce flexible and light-weight products. However, organic semiconductors do not always display the same properties of classical bulk polymers: indeed, poor ductility and low viscosity of solutions is often observed in these systems.1–3

These limitations can be overcome by employing blends of insulating and semiconducting polymers, which have been demonstrated to display favourable rheological and mechanical properties without negatively affecting the electrical performances of the produced devices. Indeed, both organic field-effect transistors and organic solar cells have been successfully fabricated with

this approach.4–7 To fully exploit the potential of these blends it is crucial to understand the crystallization processes of the various components in such blends. Here, we will focus on blends comprising an electrically insulating material, high-density polyethylene (HDPE), blended with a range of donor materials or donor:acceptor combinations. We will explain how introduction of an insulating polymer is affecting the semiconducting species during the solution deposition via blade and wire-bar coating using information obtained from a combination of methods including grazing incidence wide-angle X-ray scattering (GIWAXS), grazing incidence small-angle X-ray scattering (GISAXS), optical microscopy and in-situ UV-vis spectroscopy. Thus, we will show how the crystallization and intrachain order of the semiconducting polymer are optimally preserved provided that the semiconductor is allowed to crystallize before the insulator.

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NiO/MAPbI3-xClx/PCBM a Model Case for an Improved Understanding of Inverted Mesoscopic Solar Cells

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The basic photovoltaic mechanisms of solar converting device bearing mesoscopic (Ms) NiO, MAPbI3-xClx or MAPbI3 and PCBM as active components is investigated. Efficient hole transfer from either perovskites to the Ms NiO is demonstrated, implying a fundamental difference between this "inverted" architecture and the majorly investigated n-type one.1-3 As the charge transport is occurring in the Ms matrix, specific solutions are suggest for the overcoming the intrinsic limitations of this class of devices. The nickel oxide used has been thoroughly investigated by X-ray diffraction, by electrochemical characterization and spectroscopy UV/Vis/NIR: the direct band gap energies is estimated to be 3.87 eV and Mott-Schottky plots, measured from dark electrochemical impedance spectroscopy showed negative slopes of 1/Csc2 vs applied potential, indicating that the Ms NiO films suitably behaved as p-type semiconductors. Object of the present study is the comparison between MAPbI3 and MAPbI3-xClx perovskites embedded in "inverted" solar cells employing NiO as p-conducting electrode: differences in their photo-chemical properties are exhaustively investigated by photo-physical characterization. Perovskites have been processed through the same procedure: in our comparative study MAPbI₃xClx and MAPbI3 are both spin-coated in one-step from the precursor solution of either PbCl2 or PbI2 with MA in dimethylformamide (DMF). As expected, SEM imaging shows that the coverage and morphology of the two perovskites onto NiO are similar; light harvesting properties for the two perovskite layers on NiO are comparable as well, as evidenced from the UV-vis absorption. Current-voltage (J–V) characteristics in dark and under illumination: from the J–V curve measured under standard AM1.5G conditions, the Jsc, Voc, fill factor and power conversion efficiency (PCE) are determined as 5.7 mA cm-2, 0.89 V, 0.56, 2.9%, and 6.8 mA cm-2, 0.81 V, 0.49, 2.7% for the MAPbI3-xClx and MAPbI3 respectively.

Holes injection and transport through NiO mesoporous film is verified to be the dominant mechanism of charge collection, in contrast to what observed for electrons in mesoporous n-type TiO₂-based devices.¹ Consequently, efforts to achieve efficient perovskite p-type solar cells, based on NiO hole acceptor media, should be devoted to reduction of the NiO thickness and to the optimization of the NiO/perovskite interface. Possible solutions could be the implementation of specific mixed halide perovskite deposition techniques to obtain very smooth and uniform films, such as the double-step deposition or the employment of orthogonal solvents, which would allow making the NiO and PCBM extracting layers as thin as possible. A fine optimization and engineering of NiO-based solar cells, passing through the comprehension of their basic PV mechanism, would lead in the future to high efficient devices, combined with high voltages and long term stability.

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Influence of Porphyrinic Structure on Electron Transfer Processes at the Electrolyte/Dye/TiO2 Interface in PSSCs: a Comparison between meso Push–Pull and β -Pyrrolic Architectures.

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Time-resolved photophysical and photoelectrochemical investigations have been carried out to compare the electron transfer dynamics of a 2-\beta-substituted tetraarylporphyrinic dye (ZnB) and a 5,15-meso-disubstituted diarylporphyrinic one (ZnM) at the electrolyte/dye/TiO2 interface in PSSCs (Porphyrin Sensitized Solar Cells). Although the meso push-pull structural arrangement has shown, up to now, to have the best performing architecture for solar cell applications, we have obtained superior energy conversion efficiencies for ZnB (6.1%) rather than for ZnM (3.9%), by using the I-/I3--based electrolyte. To gain deeper insights about these unexpected results, we have investigated whether the intrinsic structural features of the two different porphyrinic dyes can play a key role on electron transfer processes occurring at the dye-sensitized TiO2 interface. We have found that charge injection yields into TiO2 are quite similar for both dyes and that the regeneration efficiencies by I-, are also comparable and in the range of 75-85%. Moreover, besides injection quantum yields above 80%, identical dye loading, for both ZnB and ZnM, has been evidenced by spectrophotometric measurements on transparent thin TiO2 layers after the same adsorption period. Conversely, major differences have emerged by DC and AC (electrochemical impedance spectroscopy) photoelectrochemical investigations, pointing out a slower charge recombination rate when ZnB is adsorbed on TiO2.

Nanosecond spectroscopy and time-resolved single photon counting apparatus evidenced similar charge injection and regeneration efficiencies. Identical dye concentrations were measured onto transparent thin TiO2 layers by spectrophotometric evaluation of dye coverage, ruling out any possible influence of loading degree on recombination kinetics. The origin of the higher efficiency of DSSCs based on ZnB appears to be ascribed, on the basis of Electrochemical impedance spectroscopy (EIS) investigation, to an intrinsic superior passivation of the TiO2 surface against charge recombination involving electron accepting species of the electrolyte. A superior screening effect, as well as reduced π -staking aggregation, are related, as shown by computational modeling, to the higher steric hindrance of the tetraarylporphyrinic architecture of the β -substituted dye, arising from the presence of four bulky tert-butyl substituted aryl rings surrounding the porphyrinic core. Conversely, the meso disubstituted push-pull diarylporphyrinic dye ZnM features a lower sterical crowding and the presence of push-amino group which may promote the formation of adducts with I3-, favouring either oxidative quenching of the excited state of the dye or recombination processes with the electrons of the photoanode, because of an increased local surface excess of I3-. Hence, the better performance of DSSCs based on ZnB with respect to ZnM, reasonably depends on a significant reduction of the recombination rate with the oxidized redox mediator rather than on differences in regeneration efficiency or charge injection yield.

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Highly Efficient π -Extended DSSC dyes: Synthetic approach, primary characterization and device testing aspects

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The communication will mainly concentrate on the design rules and the synthetic approach followed to obtain two DSSC dyes characterized by a structural extension of the π -bridge. The two organic materials have been conceived with a D–A– π –A structure in which the donor is a triarylamine group, followed by a dithienyl-benzothiadiazole chromophore to which an extension constituted by an ethynylene-thiophene (G1) or ethynylene-benzene (G2) π -spacer is covalently linked. The anchoring moiety is assured by a cyano-acrylic terminal group.

Starting from a density functional theory study it has been possible to model the absorption profile of the dyes and support the synthetic effort that will be described in detail, also with an eye to the constraints imposed by its dissymmetric nature.

The primary characterization (ESI-MS, NMR, UV-Vis) will also be addressed in the presentation along with a solvatochromic study evidencing the absence of any notable hypsochromic shifts as a consequence of deprotonation. A full electrochemical investigation points out in particular a remarkable stability of the materials.

The presentation will be completed by describing a set of experiments pointing out the high performances of the dyes liquid electrolyte DSSC devices and in particular that the structural modification of the π -spacer mainly increases the electron lifetime of G2 with respect to G1 boosting its power conversion efficiency that reaches values of 8.1%. These results are comparable to those recorded for N719 and are higher with respect to literature congeners, indicating π -bridge extension as a viable strategy for improving the dye molecular architecture.

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'Darker-than-Black' PbS Quantum Dots: Enhancing Optical Absorption of Colloidal Semiconductor Nanocrystals via Short Conjugated Ligands

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Colloidal quantum dots (QDs) are among the most attractive light-harvesting materials to be exploited for solution-processed optoelectronic applications. To this aim, replacement of the bulky electrically-insulating ligands at the QD surface coming from the synthetic procedure is mandatory. Here we show that suitable QD surface modification with short conjugated organic molecules permits to enhance light absorption of QDs, while preserving good long-term colloidal stability. Indeed, rational design of the pending and anchoring moieties which constitute the replacing ligand framework leads to broadband increase of the optical absorbance larger than 300 % for colloidal PbS QDs also at high energies (> 3.1 eV), despite previous reports on size independence of the absorption coefficient. We attribute such a drastic absorbance increase to ground-state ligand/QD electronic coupling, as inferred by density functional theory calculations; moreover, our findings suggest that the optical bandgap reduction commonly observed for PbS QD solids treated with thiol-terminating ligands can be prevalently ascribed to 3p orbitals of anchoring sulfur atoms which mix with the highest occupied states of the QDs. Here we demonstrate that organic ligands and inorganic cores are inherently electronically coupled materials which give rise to peculiar chemical species displaying emerging (optical) properties that cannot be described as the mere sum of those of the ligand and QD components. Our simple and effective approach to enhance solar-light absorption of colloidal QDs could be thus exploited for the design of light-harvesting systems to be applied in solution-processed photovoltaic and photodetection applications.

Combined Strategy to Realize Efficient Photoelectrodes for Low Temperature Fabrication of Dye Solar Cells

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We implemented a low-temperature approach to fabricate efficient photoanodes for dye-sensitized solar cells, which combines three different nanoarchitectures, namely, a highly conductive and highly transparent AZO film, a thin TiO2-blocking layer, and a mesoporous TiO2 nanorod-based working electrode. All the components were processed at T \leq 200°C. Both the AZO and the TiO2 blocking layers were deposited by reactive sputtering, whereas the TiO2 nanorods were synthesized by surfactant-assisted wet-chemical routes and processed into photoelectrodes in which the native geometric features assured uniform mesoporous structure with effective nanocrystal interconnectivity suitable to maximize light harvesting and electron diffusion. Because of the optimized structure of the TiO2-blocking/AZO bilayer, and thanks to the good adhesion of the TiO2 nanorods over it, a significant enhancement of the charge recombination resistance was demonstrated, this laying on the basis of the outstanding power conversion efficiency achievable through the use of this photoanode's architecture: a value of 4.6% (N719) was achieved with a 4- μ m-thick electrode processed at T = 200°C. This value noticeably overcomes the current literature limit got on AZO-based cells (N719), which instead use Nb-doped and thicker blocking layers, and thicker nanostructured photoanodes, which have been even sintered at higher temperatures (450-500°C).



0.3 0.4 0.5 0.6 Applied Bias (Volt)

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An engineered co-sensitization system for highly efficient dye solar cells

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Novel co-sensitizers have been structurally tailored and implemented in multi-sensitized devices demonstrating synergic efficiency enhancement. A main D-A- π -A dye and dithienyl-benzothiadiazole-based co-sensitizers were selected with synergistic properties: complementary spectral response and suitable molecular sizes; this novel co-sensitization system simultaneously provide the reduction of the intermolecular quenching phenomena across the anchored dyes as well as the optimization of the light harvesting capability of the photoelectrode.

A noticeable improvement of the photovoltaic performance has been demonstrated with respect to the sum of the performances of the best single-dye cells and an as high efficiency as 7.84% has been recorded at 1 sun illumination.



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Dibenzofulvene-based dyes for efficient DSSCs.

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Dye sensitized solar cells (DSSCs) represent one of the most promising next-generation photovoltaic devices. These devices have been attracting considerable attention due to high

performance and low-cost production. Dyes as photosensitizers are one of the most important components influencing the photovoltaic performances of DSSCs, because they determine the photoresponse range of the device and initiate the primary steps of the photon absorption and the subsequent electron transfer process. In addition to conventional Ru-complex sensitizers, metal-free organic dyes have also been utilized as sensitizers in DSSCs, and the photovoltaic performance of DSSCs based on organic-dye sensitizers has been improved by careful molecular desi



sensitizers has been improved by careful molecular design. [1-3]

We have designed and synthesized three novel organic dyes containing two donor moieties bonded to the dibenzofulvene core Fig.1, with several thiophene spacer-linker forming a 2D- π -A push-pull system, to improve solar-cell performance of the solar cells. The DSSCs based on the **TK3** dye showed high power conversion efficiency of 7.45%.

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Low temperature sequential deposition of ZnO:Al/TiO2 films by reactive sputtering for photoanodes in Dye Sensitized Solar Cells.

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Dye Sensitized Solar Cells photoanodes were prepared at temperature <150°C by sequential deposition of ZnO:Al (AZO) and porous TiO2 films using pulsed DC magnetron sputtering processes - .

AZO films were obtained by a co-sputtering method, from ZnO and Al targets in a cofocal geometry, at T=130-140°C. X-Ray Diffraction analyses suggest the formation of typical wurztite structure. The content of Al, monitored by X-ray Photoelectron Spectroscopy, is 2% as desired, the transmittance is ~ 85% and the resistivity is ~ 9 m Ω ×cm. The AZO films were thus used as TCO (transparent conductive oxide) substrates.

Deposition of TiO2 films on AZO was performed using a customised grazing incident geometry for the Ti target. In this unusual geometry , the deposition parameters were accurately optimized. To obtain a porous film, the process was calibrated on the basis of the semi-empirical model of Thornton. Cathode-anode distance and gases flow were tailored to obtain the best deposition rate value and to optimise the layer porosity. Particularly, using a low flow rate of O2 (2 sccm) allowed increasing the deposition rate to 5nm/min. This behaviour is explained with the establishment of a double plasma regime during deposition, a metallic sputtering regime near the Ti cathode (blue plasma) and a reactive deposition region near the anode (pink plasma). Deposition was performed at room temperature, the working pressure was set at 9 mTorr and the discharge power used was 140 W. The SEM images reported in Fig. 1 shows that a porous TiO2 film was deposited having an amorphous structure (XRD). The TiO2 crystallization in the anatase polymorphism was induced by annealing the sample at 500°C for 30 minutes in dry air . A preliminiray study on the functionalization of this TiO2 mesoporous structure was carried out using the N-719 dye. UV-vis and XPS analysis suggest the anchoring of dye molecule on TiO2 surface via carboxylic groups.



Fig. 1 SEM image of TiO2 mesoporous film deposited

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Highly stable gel electrolytes for dye solar cells based on in-situ cross-linkable iodopropylbranched polydimethylsiloxanes

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synthesis of cross-linkable We present the of а novel class poly[(3-Nmethylimidazoliumpropyl)methylsiloxane-co-dimethylsiloxane]iodides which have been successfully implemented as quasi-solid electrolytes for dye solar cells. They have been injected in the cell in the state of viscous liquids, which were allowed an intimate pore-filling of a few-um thick mesoporous TiO2 electrode. Once the cell has been filled, gelation can be made to happen at relatively low temperature and the polymeric gel turns into a solid membrane. A surprisingly outstanding electrochemical behavior has been revealed from a series of in-situ electrochemical analysis: these electrolytes go through an exponential increment of the ionic conductivity as the cross-linking reaction goes on and the viscous gels turn into a 3D solid network.

Smart modulation of the optical transmittance in dye-sensitized photovoltachromic devices

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A photovoltachromic cell may potentially act as a complex artificial skin, by generating electric energy as a photovoltaic system but even "perceiving" small variations in external radiation and controlling the energy fluxes by means of a smart variation of their optical transmittance. Several different combinations of dyes (basically characterized by complementary absorption spectra) and electrochromic materials (both produced by colloidal routes and by plasma enhanced laser deposition techniques) have been explored along with several specific device architectures.

Ruthenium metal complex-graphene nanohybrid system

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A novel nanostructured graphene hybrid was synthesized via functionalization of reduced graphene oxide (RGO) with ruthenium metal complex [Ru(bpy)₂(bpy-Ph-NH₂)][PF₆]₂. For this purpose, a ruthenium bispyridyl complex bearing a phenylamino group was synthesized and diazotized to isolate its tetrafluoroborate diazonium salt. A suspension of RGO in N-cyclohexyl-2-pyrrolidone was reacted with the diazonium salt to obtain the functionalized material. The resulting hybrid was characterized by UV-visible spectroscopy and thermogravimetric techniques. The results indicate the possibility of attachment of metal complex to RGO. This is the first wet chemistry approach to directly functionalize RGO with a ruthenium metal complex diazonium salt. Further, preliminary photo-physical experiments confirmed photo-induced electron transfer from the metal complex to graphene which makes it an interesting substrate, especially, as antenna system for photovoltaic applications.



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New Insight on the Role of Polymer in Hybrid PbS Quantum Dots Solar Cells *Rosanna Mastria*, ^{1,2} *Aurora Rizzo*, ^{1,3} *Carlo Giansante*, ^{1,3} *Olle Inganas*, ⁴ *Giuseppe Gigli*^{1,2,3}

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Abstract

Hybrid solar cells based on lead sulfide colloidal quantum dots (PbS QDs) and semiconducting polymers have not yet reached high efficiency if compared to their all-inorganic colloidal nanocrystal counterpart [1]. In most of such hybrid systems the non-optimal type II band offset between nanocrystals and the host polymers, e.g. polythiophenes or poly-p-phenylenevinylene, hinders the efficient separation of the photo-generated electron-hole pair in long-lived charge carriers [2]. In the last few years, the majority of research effort has been devoted on the polymer-HOMO level engineering aiming to obtain a staggered energy level alignment with PbS QDs [3]. More recently, the possibility for polymer/PbS QDs hybrid solar cells to deliver a photocurrent in the absence of an ideal type II heterojunction has been hypothesized [4] and has opened a novel path towards device improvement [5]. In this scenario, we investigate the role of the polymer in PbS QDs based hybrid systems with comparable film morphologies, exploiting the photovoltaic behavior of five semiconducting polymers that exhibit unsuitable HOMO-HOMO alignment and diverse LUMO-LUMO offsets (from 0.2 eV to 1.1 eV) with PbS QDs. Photoinduced absorption (PIA) spectra and the steady state/transient photoluminescence reveal an efficient polymer exciton quenching, sign of either electron or exciton transfer phenomenon. Furthermore such a quenching is very efficient for higher LUMO-LUMO polymer-PbS offsets, up to 95% for 1.1 eV, and this behavior is reflected in a higher photocurrent of the actual device. Our findings suggest that in hybrid polymer/PbS QD systems LUMO-LUMO offset is more crucial than HOMO-HOMO and offer a new paradigm for the design of semiconducting polymer to be integrated in highly efficient solar cells.

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Shape-tailored WO_{3-x} nanocrystals for novel multifunctional photoelectrochemical devices

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With the aim of building high-performance photo-electrochemical devices for storage and energy conversion, we have recently addressed synthetic development of a novel class of self-doped semiconductor nanomaterials capable to simultaneously exhibit plasmonic and electrochromic behavior. Nanoscale stoichiometric tungsten oxide (WO₃) is acknowledged as one of the most promising electrochromic material, while also being utilizable as photocatalytic, photoluminescent and gas sensing platform¹. Moreover, its nonstoichiometric oxygen-deficient counterpart (WO_(3- δ)) can accommodate intense localized surface plasmon resonances (LSPRs) leading to intense optical absorption bands due to excess free electrons in the conduction band.^{2,3}

Here we introduce a one-pot colloidal route to achieve size- and shape-tailored $WO_{(3-\delta)}$ ultrathin 1D nanocrystals characterized by an unusual hemi-tubular shape, showing strong and tunable LSPRs resonances at NIR to mid-IR frequencies depend ending on the nanocrystal aspect ratio. By a mild sintering process the pristine oxygen-deficient lattice can be eventually converted into a corresponding WO₃ structure with substantial size and shape, opening the way to fabrication of controllable all-nanocrystal made thin films. We are additionally exploring milder chemical approaches to remove the insulating capping shell and directly apply the ligand-free nanocrystals to construct thin films for plasmonic photo-electrochemical devices.⁴

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Driving perovskite growth through TiO₂ functionalization and its implications on photovoltaic devices.

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Organic-inorganic hybrid perovskites are among the most exciting and successful light-harvesting materials for photovoltaic applications.[1,2] Hybrid 3D perovskite structure consists of an inorganic framework of corner sharing octahedra framework and organic cations filling the 12-fold coordinated voids.[3] The formation of hybrid perovskite occurs spontaneously upon the mixing of the two precursors, usually either PbI₂ or PbCl₂ and methylammonium halide salt, onto the substrate. Like every self-assembly process, the control on the environment conditions and substrate are of a paramount importance to control perovskite formation and final device performance.[4-6] Here we propose exploit TiO₂ surface functionalization to guide the crystallization process of CH₃NH₃PbI_{3-x}Cl_x perovskite and to modulate its oriented growth. Most notably our approach allows obtaining similar thickness, morphology and absorption properties of the perovskite film and to finally discriminate the effect of orientation of perovskite poly-crystals on device performances.

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Effect of P3HT molecular weight on stability and photoelectrochemical parameters of solid-state provskite solar cell

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Photovoltaics based on organic-inorganic perovskites offer new promise to focus on contemporaneous energy and environmental issue. During the past decade Poly (3-hexylthiophene) P3HT has become one of the most use component in organic electronics, which is related to high hole mobility and low cost. In this research, we have investigated the effect of different molecular weights of P3HT as a hole transport materials (HTMs) with same concentration and same thickness on the performance of the solid state provskite solar cell. On the other hand, we have also checked the best method for P3HT and perovskite deposition (one step and two step). J-V measurements of the solar cells are investigated under AM1.5G irradiation and photoelectrochemical parameters like open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF) and the overall efficiency, are evaluated. In totally, by increase of the molecular weight, solar cell stability and Jsc are enhanced and efficiency, FF and Voc are decreased. The stability of the devices are measured 4 times (first day and after 10, 20 and 45 days, in room temperature and air condition).

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The Influence of Fullerenes on the Microstructure and Photophysical Properties of Polymer:Fullerene Blends

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Organic solar cell blends comprised of an electron donating polymer and electron accepting fullerene typically form a thin-film structure made up of a complex mixture of phases upon solution casting. These phases can vary greatly in: composition; order and thermodynamic stability, and are dramatically influenced by the processing history. Understanding the processes that govern the formation of these phases and their subsequent effect on the efficiency of photogenerating and extracting charge carriers is of utmost importance to enable rational design and processing of these blends. Here we demonstrate the dramatic influence of the fullerene on the crystallinity of the donor polymer, leading to the formation of a highly intermixed solid solution. The formation of this solid solution increases the exciton quenching efficiency and, terminally, the short circuit current of photovoltaic devices when present in conjunction with more phase-pure domains. These findings highlight the striking influence of fullerene during solution casting and provide clear guidelines from which control of the mixture of phases can be attained to improve the performance of polymer:fullerene solar cells.

12x17cm² glass-frit sealed smart window prototype integrating DSSC and electrochromic screen printed sections

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Electrochromic (EC) glazing as smart window systems can perform a number of important functions in building envelops allowing dynamic control of the amount of solar radiation entering the building, and enhancing the human comfort. They can provide solar light glare control and variable visual connection with the external word as well as passive solar energy gain by infrared radiation absorption. Panels containing DSSCs that generate the power supply for the electrochromic sections are an example of self-sustaining smart window that can as well have a good architectural expression. Our activity focuses on the fabrication of time-durable dye sensitized solar cell (DSSC) and electrochromic devices contained in the same panel. In order to ensure low production costs the active layers of the different sections were deposited by screen printing, a low-cost manufacturing process. The electrolytes used for the DSSC and EC sections are ionic liquid based. Glass frit was used as the sealing material to obtain an industry-standard durable device.

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Solid state perovskite-based photovoltachromic device

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In the last years, the energy market registered a growing demand of new photovoltaic (PV) technologies, suitable for building integration. In particular, semitransparent PV modules are strongly desired to replace a number of architectural elements commonly made with glass, such as windows and skylights. Recently, perovskite solar cells have been demonstrated as a new photovoltaic material. In fact, semitransparent perovskite-based devices can achieve high photoconversion efficiency and remarkable transparence, on lab scale. Furthermore, they can be prepared neutral colored offering full flexibility to make aesthetically appealing building integrated PVs.

We report a completely new architecture for solid state photovoltachromic devices, capable of producing electric power by photovoltaic conversion as well as to undergo smart and homogeneous coloration and bleaching, depending on the irradiation conditions. Briefly, such a double glass device embodies highly transparent perovskite-based photovoltaic cells, a solid polymer electrolyte based on PEO-lithium salt (LiX) complex plasticized with low molecular weight PEG. The obtained electrolyte is a durable, adhesive and transparent ion conductor. A thin film of WO₃, deposited by electron beam evaporation technique, acts as a cathodic electrochromic semiconductor.

Using this device architecture, we obtained semitransparent PVCCs with respectable solar conversion efficiency of 5.5% and a smart modulation of optical transmittance higher than 20%.

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