Energy for the XXI century: challenges and opportunities

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During the 20th century world primary energy consumption has increased over 15 times, due to the massive exploitation of fossil fuels. It is rather unlikely that the 21st century will be, energetically speaking, a replica of the previous 100 years [1-2]. Besides the impending shortage of oil and natural gas supply [3] in a planet populated by 9 billion energy-thirsty inhabitants in 2050, the use of *una tantum* fossil energy resources could be limited due to environmental concerns, related to public health or anthropogenic climate forcing [4]. These scientific and technical problems are made even harder by geopolitical issues, e.g. concentration of conventional energy resources in limited regions of the world or disparity of energy distribution between affluent countries and underdeveloped nations [1]. The exploitation of new energy sources and the improvement of current energy technologies will be among the most challenging scientific endeavours of the 21st century. Photochemistry, which has been concerned with the search for renewable energy sources since its very beginning [5], can play a leading role in this effort. Research perspectives in the field will be outlined.

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Supramolecular Chemistry with Fullerenes and Carbon Nanotubes

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Fullerenes and carbon nanotubes are novel materials with interesting electronic, electrochemical and mechanical properties. Their structure, based exclusively on carbon atoms arranged in benzene rings, is ideally suited for a number of supramolecular interactions with similarly aromatic systems. During this contribution, we will report our ongoing studies on the synthesis and applications of fullerene derivatives and functionalized carbon nanotubes. In particular, the preparation and behaviour of molecular shuttles stoppered with fullerenes will be discussed, focusing on how fullerenes can be used to monitor and induce molecular motion. Also, we will show how such motion can be employed to modulate the physicochemical properties of molecules such as light-driven electron transfer events, non-linear optical properties, fluorescence, electrochemical potential and chemical stability. The organic functionalization of carbon nanotubes (CNT) offers the great advantage of producing soluble and easy-to-handle CNT. As a consequence, compatibility of CNT with other materials, such as polymers, is expected to improve. In addition, once properly functionalized, CNT become soluble in many solvents, so that their solution properties can be studied. Many functionalized carbon nanotubes may find useful applications in the field of materials science and technology, including photovoltaics. Also in medicinal chemistry carbon nanotubes are set to play an important role. To solubilize CNT, several strategies have been devised. Among these, the most successful are: 1) the covalent functionalization of *sp*2 carbons at the sidewalls with organic pendant groups and 2) the non-covalent functionalization through supramolecular interactions (e.g., π-π stacking interactions), which allows the formation of stable suspensions.

An Introduction to Molecular Wires

Professor Harry L. Anderson

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This lecture will start by introducing the concept of π-conjugation in the context of linear polyenes and polyacetylene. This will lead to discussion of Lehn’s membrane-spanning caroviologens, and thus to molecular wires connecting metal electrodes, the techniques for making electrical contact to the ends of a molecule and the factors controlling molecular conductance. The attenuation factor, β, will be introduced in the context of single molecule conductance and extended to consider photoinduced electron transfer, leading to an introduction to Marcus theory. Other techniques for measuring charge mobility and delocalisation in molecular wires will be summarised briefly, including UV-visible-near IR spectroscopy, ESR spectroscopy and time-resolved microwave conductivity. The lecture will end by discussing potential applications of molecular wires, and the motivation for investigating them.

Do you speak HCTH407/EPR-III?

P. Marsal

University of Mons, Belgium

In order to provide a deeper insight into some of the dynamic processes going on in the field of material sciences, theoretical methods has been widely used as an attractive and complementary tools to experimental techniques. In some cases, the interpretations of the experimental results are still far from being an easy task. This is where the use of theoretical tools and modelling becomes crucial. The goal of this talk will be to help the people to become more familiar with the concepts hidden behind this "hermetic" theoretical language. A brief overview of computational chemistry will be presented from various theoretical approaches and define all the physical concepts and approximations used to build them, up to state-of-the-art methods such as Density Functional Theory (DFT) techniques. In a second part, we will see the benefit of a combined 'Theory-Experiment' approach on several examples to show that a theoretical approach can provide accurate numbers but also can give rich insight of the driving forces of a physical property. In all cases only a continuous feedback between theory and experiment will allow refining the existing models.

Density Functional Theory Calculations of Organic Molecules Adsorbed on Metal Surfaces

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Density functional theory (DFT) has become the method of choice to perform "first principles" electronic structure calculations for many systems. Its relatively low computational cost, good scalability and the easy availability of existing programs have led to its widespread use. This lecture will attempt to give an overview of the use of density functional theory and related calculations to study the adsorption of reasonably sized organic molecules (10-100 atoms) on the surfaces of transition metals. It will discuss the properties that can be calculated and how these may be related to experimental results. In particular the interpretation and in some cases prediction of the results of scanning tunnelling microscopy, scanning tunnelling spectroscopy and surface-sensitive infra-red spectroscopy using DFT calculations is discussed. It cannot, however, be claimed the DFT is without its failings, and some of these will be addressed. There are still limitations on the size of the system which can be studied, limiting both the of size of the adsorbed molecule and introducing finite size effects. DFT is a ground state theory and as a result errors are introduced when using the vacant Kohn-Sham orbitals to probe unoccupied orbitals of a system. DFT is also known to underestimate dispersion interactions including p-p and van der Waals interactions and physisorption energies. In spite of these failings we aim to show that DFT is an indispensable tool for the investigation of the electronic structure of metal-adsorbate systems and the interpretation of related experimental data.

Supramolecular Chemistry:
From science to applications

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Today, synthetic polymers are an essential part of our life. In many applications, the performance depends very much on the structure and interactions of the polymer. Therefore, it is from an academic and industrial point of view essential to continuously expand the knowledge of structure-property relationship of functional polymers. Inspired by nature, the introduction of non-covalent interactions in synthetic polymers has become an active field of research. Such polymer materials can exhibit enhanced functionalities and performance due to their ability to self-assemble. In the presentation, several methods to use non-covalent interactions to overcome current limitations of (noninteracting) polymers will be described.

1. While high molecular weight polymers are required in many applications to achieve the desired properties, the handling of these polymers is difficult due to the high viscosity in solution. Introducing hydrogen bonding and inter-polyelectrolyte complexes by adding additional building blocks can induce phase-separation of dispersed compartments of high molecular weight polymer keeping the low viscosity of the solution.
2. Phenylene-thiophene-thiophene-phenylene (PTTP) derivates are representing an interesting class of materials which can be used in organic field effect transistor. The packing of the PTTP derivates is essential for the performance of the device. By adding specific functional groups to the PTTP, the self-assembly of the molecules on a molecular level can be controlled and manipulated.

Unconventional Lithographic Techniques applied to supramolecules

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Here we present how a bottom-up nanofabrication techniques can be applied to supramolecules and how they can improve some properties of thin solid films via nanostructuration. We describe Bottom-Up approach to nanofabrication, From serial (Scanning probe nanolithography) to parallel (stamp assisted), the role and application of dewetting in nanofabrication and a detailed description of some unconventional lithographic methods such as Lithographically controlled wetting (LCW)[1], and spatial controlled dewetting applied to supramolecules. LCW [2] allows to pattern soluble materials with nanometer-sized structures in single step and in a few seconds. We demonstrate patterning nanostructures like droplets, stripes and fibers, with size feature less than 100 nm, for a variety of materials relevant to organic electronics: conjugated oligomers and polymers, liquid crystals, molecular magnets and spin crossover compounds rotaxanes. We show how the nanostructuration by LCW can induce self-organization. In the second part we demonstrate a direct application of spatially controlled dewetting (SCD) [3]. In SCD, dewetting can be induced and controlled both in space & time by Atomic Force Microscopy4 or by rigid stamp. In order to illustrate this control we used SCD to generate, in few seconds, highly ordered patterns with a resolution of 40 nm and to write some digital information on organic thin solid films.

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Charge transport along molecular wires

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A method to measure the mobility of charge carriers along molecular wires will beintroduced. The molecular wires are isolated from each other by dissolving them in an organic solvent. Charge carriers are generated by irradiation with high-energy electrons from a Van de Graaff accelerator. The mobility of charge carriers moving along the molecular wires is obtained from time-resolved microwave conductivity measurements. The charge carrier mobility is found to strongly depend on the structure of the molecular wire. Rotational disorder of the monomer units in the wire has a significant negative effect on the mobility. For planar wires of phenyl units a very high mobility approaching that for inorganic semiconductors has been realized. It will be demonstrated how the experimental findings can be rationalized by quantum chemical calculations. A tight-binding (Hückel) model to describe the charge carrier will be presented. The quantum mechanical description of the charge carrier is combined with a classical description of the nuclear degrees of freedom. It will be shown how the parameters relevant to charge transport (electronic couplings, site-energies and reorganization energies) can be obtained from electronic structure calculations such as density functional theory (DFT).

Ionic Liquids in Supramolecular Chemistry and Plastic Electronics

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Ionic Liquids (ILs) are defined as low melting point salts (<100 ºC). They are organic salts liquid at room temperature, usually composed of organic asymmetric cations and inorganic anions. IL science and technology constitutes a rapidly expanding topic of research as shown by the exponential increase of scientific publications due to the originality and unique properties of these chemical compounds. The most prominently exploited are: negligible volatility, high chemical, thermal and electrochemical stability, high thermal and ionic conductivity, tuneable polarity, miscibility and solubility. Figure 1: Left side: Number of scientific publications related to Ionic Liquids during the period from 1998 to 2007. Right side: Chemical structure of common ionic liquids. In this lecture we will show the recent advances in the use of ionic liquids in suparamolecular chemistry as well as the design of materials for plastic electronics. At this respect, we will put an special focus in the last developments which are showing the excellent performance of ionic liquids as electrolytes in different devices such as solar cells, lithium batteries, electrochromic devices, light-emitting electrochemical cells and supercapacitors.

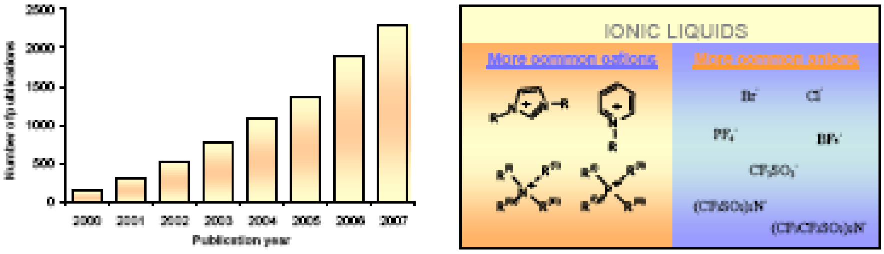

Figure 1. Left side: Number of scientific publication related to Ionic Liquids during the period 1998 to 2007. Right side: chemical structure of common ionic liquids.

Molecular and Supra-Molecular Self Assembly at Surfaces: Towards Adressable Multi-stable Devices

M. Stoehr, N. Wintjes, H. Spillmann, S. Schintke, A. Baratoff, D. Bonifazi,
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One of the key challenges in molecular machines and devices is the reproducible assembly of functional units in an addressable way, e.g. in 2D arrays at surfaces. By combining concepts of supra-molecular chemistry [0] and surface science, increasingly complex functional layers have been manufactured and explored. Selective molecular interaction is the generic origin of molecular self assembly [1] and distinctively different mechanisms have been identified: Selective chemical bonding [2], conformational bi-stability [3], and 2D phase behaviour [4] produce distinctly different functional layers. Binary molecular systems which involve longer range dipole forces and entropic mobility provide the basis for an increased periodicity [5]. In conjunction with a conformational mechanism the spacing between individual supramolecular units has very recently been increased to 7.2 nm [6]. Beyond supra-molecular assembly, extended networks have been created by a thermally activated chemical reaction [7] and have been used as a template for supra-molecular organisation of ad molecules [8,10]. 'Random walk' analysis reveals conclusive statements on the host-guest interaction of pores and guest which can be related to early work by Mott and Peierls and also to the Host-Guest interaction within Zeolithes. Ultimately, the assembly of addressable supra-molecular rotor-stator systems and their Arrhenius type activation of libration is described which tops in the demonstration of a locally actuated supra-molecular rotational switch [11,12]. Most recently, the successful assembly of extended molecular layers on insulator thin films has been demonstrated [9]. All these examples have in common that the supra-molecular structures are extremely well defined on a level which is impossible to reach by conventional top-down assembly techniques. The physics and chemistry of these unprecedented addressable systems provides insight into mechanic and electronic 'function' on a single molecular scale.

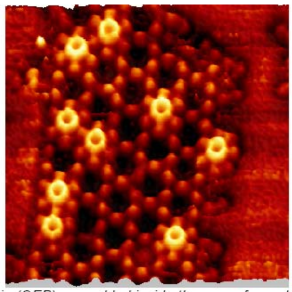

Figure 1: Octa-ethyl-porphyrin (OEP) assembled inside the pores formed by a reactively formed network of resonant hydrogen bridged perylene. At room temperature STM reveals ring like structures due to confined libration.

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Functional Molecules for Hierarchical Self-Assembly and Use in Optical and Electronic Devices

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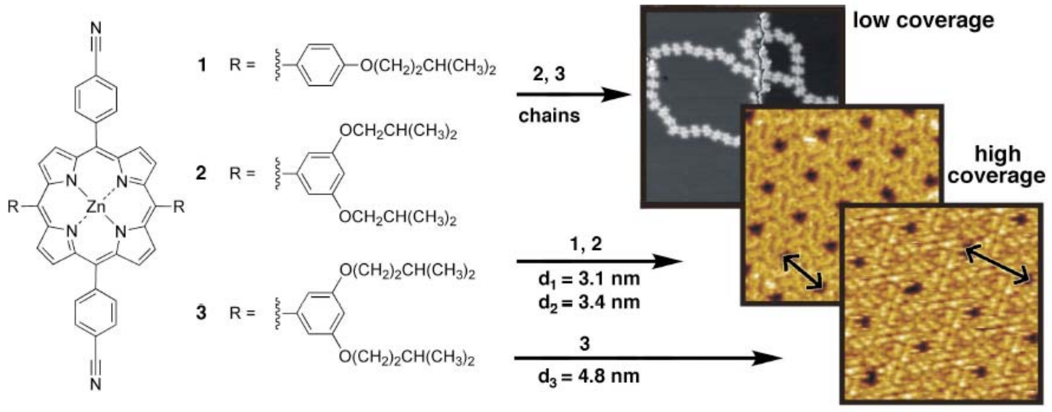
Donor-substituted cyanoethynylethenes as donor-acceptor chromophores have been synthesized for third-order non-linear optical (NLO) applications. Some of these molecules exhibit record-high optical non-linearities. The robust and compact molecules can be sublimed without decomposition, yielding thin films which may be used for the development of optica devices. A series of oligoporphyrins and fullerene-oligo(Zn(II)porphyrin) conjugates was prepared and their electrochemical and photophysical properties, as well as their conformational preferences investigated. The electrochemical results show that all dyads have an exceptional multicharge storage capacity due to the large number of reversibly exchangeable electrons. Depending on the type of inter-porphyrin linkage, photophysical studies showed efficient photoinduced electron-transfer, but also unprecedented energy-transfer. The exceptional photophysical and electronic properties of such compounds may render them suitable for applications as conductive organic materials, near-infrared dyes, NLO materials, molecular wires, or other molecular devices. Supramolecular porous networks can be grown on monocrystalline surfaces from substituted porphyrins that self-assemble into various 1D- and 2D-structures (see scheme). In recent years, we intensively employed the supramolecular cyanophenyl-cyanophenyl interaction motif to direct self-assembly on metal surfaces. We now focus on interactions that have not been employed on surfaces so far, e.g. halogen bonding and phenyl-pentafluorophenyl interactions, which are promising in view of increased interaction energy and, thus, stability of the resulting networks.



Self-assembly of three different porphyrin derivatives on Cu(111) surfaces into molecular chains and networks

Vibrational Spectroscopy on Supramolecular Systems

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Self-assembled molecular networks can be very effectively characterized by their vibrational properties, because during assembly, changes in both molecular symmetry and bonding characteristics can occur. I will present an introduction to molecular symmetry effects ovibrational spectra, the changes expected by intermolecular bonding, and to the applied techniques to both bulk samples (infrared transmission and reflectance, Raman scattering) and surface layers (single- and multiple-bounce ATR, IRRAS). I will demonstrate the application of these methods on supramolecular systems formed by hydrogen bonds.

Radiation-based Surface Engineering for Ordered Molecular Films

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The structure of molecular films, grown or deposited onto solid substrates, may be drastically influenced by the physical and chemical structure of the surfaces. In particular for films deposited from solutions, a number of features, including the presence of specific chemical groups at surfaces, their charge state in solution, the existence of electrical domains, as well as micro- or nanoscale morphology has been demonstrated to critically affect the molecule-substrate interaction. Thus, depending on the physical and chemical nature of the surfaces, ordering processes at the solid-liquid interfaces may be induced and /or controlled. The structure of the first interacting molecular layers, in turn, may influence the molecular organisation of the whole deposited films, propagating the surface-induced conformational or orientational effects. In this lecture, a non-exhaustive summary will be provided about the use of radiation-based techniques to modify in a more or less specific way the chemical structure and the physical properties of inorganic as well as organic surfaces. The attention will be focused in particular on the use of low-energy ion beam techniques, plasma- and UV-based methodologies, as these are among the best established methods to induce surface modification/reorganisation and to add specific functional groups or also ultra thin functional layers on surfaces. The use of these techniques to modify the nature and concentration of specific chemical groups at surfaces, the surface free energy (i.e., wettability), the electrical properties and the micro- and nanoscale morphology will be addressed. Examples of the effect of the modified surface properties on the structure of thin and ultra thin molecular films will be discussed.

Organic light-emitting and photovoltaic devices: basic structure, fundamental processes and their optimisation, also with reference to the use of supramolecular materials

Franco Cacialli

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I will review the fundamentals of organic light-emitting and photovoltaic devices with particular emphasis on light-emitting diodes, LEDs, light-emitting electrochemical cells (LECs), and excitonic solar cells. The lecture will be structured in 4 parts covering respectively: (a) Organic LEDs: after a brief introduction to their historical development and the general device architecture, I will introduce the fundamental processes taking place during electroluminescence (EL). This will be followed by a description of the physical parameters used to characterise such devices (e.g. max luminance and efficiencies) and of the strategies used for the optimisation of the device performance. This will include a section dedicated to the use of supramolecularly engineered materials, and in particular threaded molecular wires (TMWs) for the increase of the luminescence efficiency via suppression of detrimental intermolecular interactions.(b) LECs: this part will cover the fundamental idea at the basis of LECs and after reviewing the most important differences with LEDs, will cover briefly the different interpretations for the behaviour of different complex devices whose commercial exploitation is still hampered by stability problems. (c) Electrodes engineering: A special part of the lecture will be dedicated to the issue of electrodes engineering that is crucial to all polymer devices, not only light-emitting, but also photovoltaic diodes, PVDs, and field-effect transistors, FETs. The use of electroabsorption spectroscopy for the analysis of the energy level line-up at metal-semiconductors interfaces will be illustrated. (d) Organic photovoltaic diodes, PVDs. The final part of the lecture will be dedicated to the introduction of the fundamentals of organic photovoltaic cells, and to the processes that are at the basis of their operation.

Solution Zone Casting – a Method for Fabrication of Oriented Layers for Optoelectronic

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Achievement of macroscopic scale long-range order (and thus orientation) in organic conductors and semiconductors is of a great importance in their applications in electronics and optoelectronics. Obtaining sufficiently large single crystals is usually very difficult or impossible. Thin layers of organic materials with anisotropic structure and properties in the direction perpendicular to the substrate can be obtained by methods such as Langmuir-Blodgett technique or, to some extent, by vacuum deposition. Achievement of long range order and orientation *in the plane* of the substrate is much more difficult, and usually requires the use of external stimuli (e.g., mechanical deformation) or appropriately patterned substrates (for solution casting). This presentation will describe an alternative method for the solution casting based fabrication of oriented anisotropic layers of molecular materials which does not require patterned substrates. In this method, originally developed in CMMS PAS , the solution is continuously supplied onto the substrate withdrawn at a controlled rate and the solvent evaporates from the surface of meniscus formed between a flat nozzle and the substrate. Due to the presence of the gradient of the solute concentration, its crystallization (or more generally the solidification) proceeds within the narrow zone localized in the meniscus. Under such conditions an anisotropic layer, with uniform long range order (orientation) extending over the centimetre scale can be directionally and continuously deposited on the substrate. I will be presented a description of the zone casting process and several examples of different materials low molecular weight conductors , discotic molecules and block copolymers which can be successfully processed using this technique. Some of these materials were already shown to have good properties as active layers in field effect transistors.

Scanning Probe Microscopies beyond imaging: a journey into the nanoscale world

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The invention of Scanning Probe Microscopies (SPMs) opened doors into the nanoscale world, and ultimately to nanotechnology. Looking at individual nano-entities such as single molecules, how they react to an external stimuli, how they move and dance on a surface, and how they recognize and talk to each other is no longer science fiction. Moreover, these nanotools allow the manipulation of individual nano-objects and enable scientists to gain a quantitative insight into their physical and chemical properties across multiple length scales. Thus they can provide crucial information for the optimization of multifunctional materials for nanotechnology. The ultimate impact of these tools will surely cover a huge range of disciplines, including materials science, (opto)electronics, medicine, catalysis, and they will offer new solutions to key problems such as energy and the environment. My lecture will review recent progress in the use of SPMs beyond imaging on soft materials,[1] with a particular emphasis on the Atomic Force Microscopy (AFM) studies of mechanical properties of isolated polymer chains rigidified by non-covalent interactions [2] and on the conducting-AFM (C-AFM) measurements of the electrical properties of monolayers and functional nanostructures.[3] In addition Kelvin Probe Force Microscopy (KPFM) [4] investigations were carried out in order to explore the electronic properties of single [5] and multi-component functional nanostructures. Moreover KPFM made it possible to map the photovoltaic activity in electron acceptor/donor blends both on the hundreds of nanometers [6] and on the few nanometers scale.[7] On the other hand, Scanning Tunnelling Microscopy (STM) provided direct insight into the perturbation of the electronic states of molecules adsorbed at surfaces. Detailed understanding on the contrast in sub-molecularly resolved STM images of a monolayer of an azatriphenylene physisorbed on graphite was accomplished relying on the assistance of quantum chemical calculations.[8] I will also show that STM is a suitable tool for the characterization, with a sub-molecular resolution, of multicomponent architectures [9], opening perspectives towards a higher control of the reactivity on surfaces.[10] Finally I will present a strategy for the fabrication of prototypes of mechano-chemical switches powered by light irradiation: Significantly, the photochemical isomerization of a new terminally thiolated azobiphenyl rigid rod, forming a single component SAM on metallic surfaces, was found by STM to be highly cooperative and to be complete over a molecular 2D crystal. [11] In the end, SPM techniques are all about the five senses. Sight is achieved by gently touching surfaces. Hearing: the acoustic response of the tip allows detailed insights into the mechanical properties of surfaces. The same tips, once functionalized with well-defined groups, can identify functional groups through molecular recognition, thus they can finally smell and taste the new and thrilling perfume and flavor of the nanoworld.[12]

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Biochemical and Therapeutical Applications of Nanotechnology

Dr. Mairena Martín

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Nanotechnology is the creation and utilization of materials, devices, and systems through the control of matter with length scales in the 1 to 100-nanometer range. Nanodevices and nanomaterials can interact with biological at fundamental, molecular levels with a high degree of specificity. By taking advantage of this unique molecular specificity, these nanotechnologies can stimulate, respond to and interact with target cells and tissues in controlled ways to induce desired physiological responses, while minimizing undesirable effects. Nanoparticles, such as gold nanoparticles and quantum dots, are the most widely used, but various other nanotechnological devices for manipulation at the nanoscale as well as nanobiosensors are also promising for potential clinical application. Therefore, nanoparticles have an important application to diagnosis and treatment of several pathologies. Nanoparticles are being used as the basis of diagnostic assays for cancer and to visualize tumor during surgery. Nanoscale optical biosensors have been proposed as biomarkers for analysis of human brain extract and cerebrospinal fluid samples from some neurodegenerative disorder as Alzheimer disease. Several technologies based on nanoparticles have also been described to facilitate drug delivery, which is important for optimizing the effect of drugs and reducing toxic side effect. Biotechnology and Nanotechnology are the most promising technologies to date. Convergence of these two technologies results in nanobiotechnology. Nanobiotechnology is playing and important role in advances in oncology, neuroscience and microbiology. Therefore, Nanobiotechnology can play an important role in the development of nanomedicine in the future. However, the study of the safety of nanoparticles will be necessary. Interactions between nanoparticles and cell membranes may play a crucial role in determining the cytotoxicity of nanoparticles as well as their potential application as drug delivery vehicles or therapeutic agents.

Ultrafast dynamics in conjugated chains

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Π-electrons confined in one dimensional space are strongly correlated, giving rise to tight bound excitons with large oscillator strengths and narrow optical resonances, large non-linear response and short lifetime. Time resolved spectroscopy is a fruitful and commonly applied tool for investigating their dynamics. Here we will review the techniques and show evidences for intra-chains properties, which can be single out due to the supramolecular architectures in the sample. Application of fundamental optical phenomena, such as light amplification and optical switching, will be discussed.

Ultrafast optoelectronic probing of charge mobility and kinetics in organic solar cells

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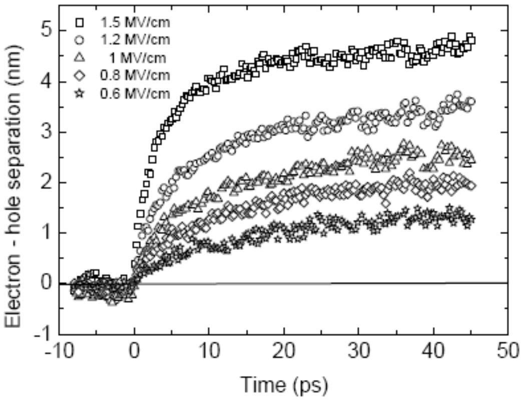
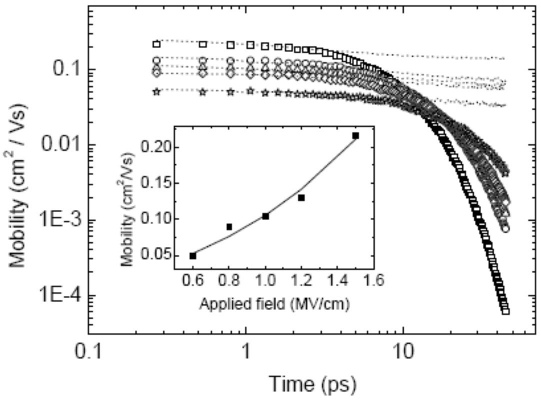
We present sub-picosecond charge mobility measurements in organic solar cells based on [6,6]-phenyl C61-butyric acid methyl ester (PCBM) with photoinduced Stark spectroscopy. This novel technique allows for monitoring the picosecond evolution of the electron – hole pair distance during the process of charge photogeneration [1][2]. Taking into account both the e – h distance and the effective field inside the photogenerated area, (both measured by the technique), picosecond charge mobility values are obtained in solar cells. PCBM is a soluble fullerene derivative extensively used in organic bulk heterojunction solar cells as electron acceptor due to its large electron mobility [3]. Films of PCBM deposited by spincoating are typically polycrystalline with crystalline grains of sub – micron size [4]. Owing to the large concentration of grains in the PCBM bulk, the majority of e - h pairs are confined inside PCBM grains during the first picoseconds after charge photogeneration. Therefore our technique probes the motion of charges inside these crystalline domains. Moreover, mobility values are obtained without current extraction being independent of device architecture and mesoscopic organization. They are intrinsic properties of the material, offering a direct feedback to materials scientists for the synthesis of compounds with improved charge transport properties.





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