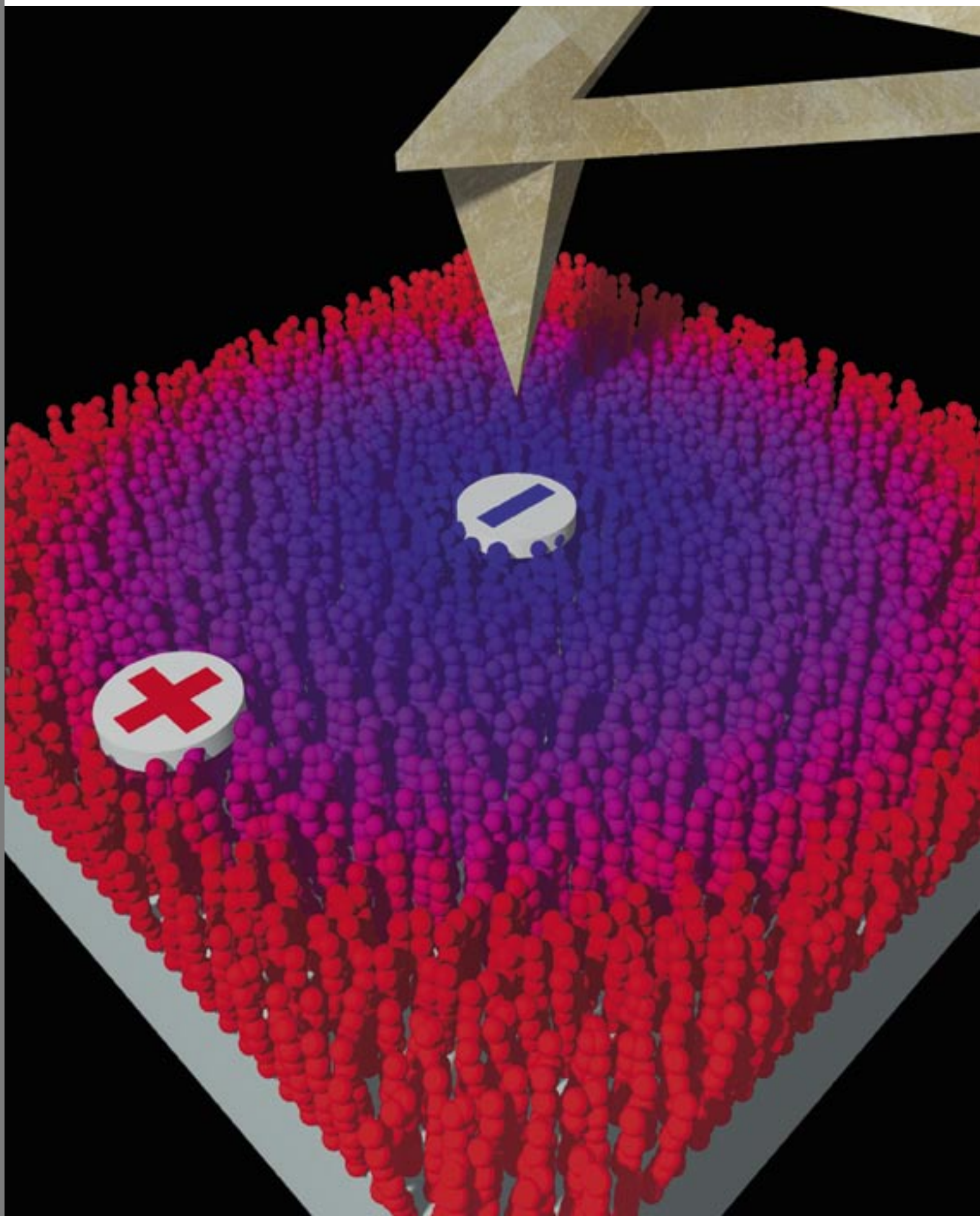


**EUROCORES Workshop on Self-Organised
NanoStructures (SONS)**

Strasbourg, France, 31 May-1 June 2007



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*** The following national funding agencies support the SONS Programme First Call**

- Fonds zur Förderung der wissenschaftlichen Forschung (FWF)
Austrian Science Fund, Austria
- Fonds National de la Recherche Scientifique (FNRS) National Fund for Scientific Research, Belgium
- Fonds voor Wetenschappelijk Onderzoek (FWO)
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Natural Science Research Council, Denmark
- Suomen Akatemia/Finlands Akademi (AKA)
Academy of Finland, Finland
- Commissariat à l'Énergie Atomique / Direction des Sciences de la Matière (CEA)
Institute for Basic Research of the Atomic Energy Commission, France
- Deutsche Forschungsgemeinschaft (DFG)
German Research Foundation, Germany
- Országos Tudományos Kutatási Alapprogramok (OTKA)
Hungarian Scientific Research Fund, Hungary
- Magyar Tudományos Akadémia (MTA)
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- Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)
Netherlands Organisation for Scientific Research, Netherlands
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Research Council of Norway, Norway
- Polska Akademia Nauk (PAN)
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- Fundação para a Ciência e a Tecnologia (FCT)
Foundation for Science and Technology, Portugal
- Slovenská Akadémia Vied
Slovak Academy of Sciences, Slovak Republic
- Consejo Superior de Investigaciones Científicas (CSIC) / Ministerio de Educación y Ciencia (MEC)
Council for Scientific Research / Ministry of Education and Science, Spain
- Vetenskapsrådet (VR)
Swedish Research Council, Sweden
- Schweizerischer Nationalfonds (SNF)
Swiss National Science Foundation, Switzerland
- Türkiye Bilimsel ve Teknolojik Kurumu (TÜBİTAK)
The Scientific and Technological Research Council of Turkey, Turkey
- Engineering and Physical Sciences Research Council (EPSRC),
United Kingdom

*** The following national funding agencies support the SONS Programme Second Call**

- Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (FWF)
Austrian Science Research Fund, Austria
- Fonds voor Wetenschappelijk Onderzoek - Vlaanderen (FWO)
Fund for Scientific Research – Flanders, Belgium
- Grantová agentura České republiky (GA ČR)
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- Consiglio Nazionale delle Ricerche (CNR)
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Council for Scientific Research, Spain
- Schweizerischer Nationalfonds
Swiss National Science Foundation, Switzerland
- Engineering and Physical Sciences Research Council (EPSRC),
United Kingdom

This workshop is supported by funds from the European Commission Sixth Framework Programme under contract n. ERAS-CT-2003-980409

Preface from the SONS Programme Coordinator

Self-Organised NanoStructures (SONS) is a EUROCORES Programme of the European Science Foundation supported by 25 National Funding Organisations*.

SONS are complex supramolecular structures that can assemble themselves through competing interactions between their components and their applications are ranging from magneto-opto-electronics, to catalysis and nano-medicine.

The first Call for Proposals was launched in 2002 and Sixteen Collaborative Research Projects (CRPs) were funded and started their research activity in 2004 and are now close to their final stage. Seven CRPs were funded after the second Call for Proposals and started their research activities in 2006.

This workshop, organised in the frame of the EMRS Spring meeting, brings together, for the first time, principal investigators and young researchers from SONS first call and second call scientific communities. The Scientific Programme of this workshop consists of 22 oral and 40 poster presentations and it will be complemented by four key-note lectures from international leaders in the field.

This joint networking activity aims to present the scientific results and latest achievements in these Programmes and the state-of-art in this area of research and will thus provide a platform for world-class leading scientists and young researchers in the field to interact.

A special thank goes to the Chair of the Scientific Organising Committee, Dr. Paolo Samorì, for his dedication and care in producing the scientific programme and to Dr. Mario Ruben for his helpful suggestions.

On behalf of the SONS Scientific Organising Committee we would like to welcome you to this EUROCORES Workshop on Self-Organised NanoStructures, and we wish you a very pleasant and fruitful workshop.

May 2007, Strasbourg

Dr. Antonella Di Trapani
SONS Programme Coordinator

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Conference Programme

Thursday 31 May 2007

8.00-8.45	Registration
8.45-9.05	Welcome address Antonella Di Trapani (EUROCORES Programme Coordinator ESF) Paolo Samori (Chair of the SONS Workshop Scientific Committee)

Session 1: Biological Chemistry

Chair: **Richard Bushby**

9.05-9.50	Giovanni Marletta (University of Catania and CSGI) Invited Lecture: Self-assembling Processes at Biological Surfaces and Interfaces
9.50-10.10	Giampaolo Zuccheri (University of Bologna, Italy) BIONICS- The programmed self-assembly of DNA as a tool for controlling the structure and function of matter on the Nanoscale
10.10-10.30	Christian Dittich (University of Basel, Switzerland) BIOSONS- Purpose and adaptability: induced self-assembly of a biological peptide motif
10.30-10.50	Duncan Sutherland (iNANO, University of Aarhus, Denmark) NANOSMAP- Utilising colloidal templates to nanopattern macromolecules over large areas for biological applications
10.50-11.10	-Coffee break-

Session 2: Synthetic Chemistry

Chair: **Pavel Kratochvil**

11.10-12.00	John E. Anthony (University of Kentucky, USA) Invited Lecture- Tuning aromatic π - π interactions for improved film morphology and device performance
12.00-12.20	Uta Schlickum (EPFL, Switzerland) FUN-SMARTs I- Supramolecular engineering with linear dicyanitrile molecules on Ag(111): 2-D chiral Kagome lattice and tuneable nanoporous metal-organic networks
12.20-12.40	Bertrand Donnio (CNRS, Strasbourg, France) LC-NANOP-Liquid Crystalline self-organization of $[\text{Mn}_{12}\text{O}_{12}(\text{RCO}_2)_{16}(\text{H}_2\text{O})_4]$ clusters derivatives
12.40- 13.00	Carsten Tschierscke (University Halle, Germany) SCALES- Complexity across length scales in soft matter
13.00-14.00	-Lunch-

Session 3: Physical Chemistry

Chair: **Jean-François Legrand**

14.00-14.45	Hans-Jorg Schneider (University of Saarbrücken, Germany) Invited Lecture-Molecular Recognition in Chemomechanical Polymers
14.45-15.05	Gunter Reiter (CNRS, Mulhouse, France) SONS-AMPHI-Long-time evolution of order on a hierarchy of lengthscales in self-organized monolayers
15.05-15.25	Peter Stepanek (Institute of Macromolecular Chemistry, Prague, Czech Republic) AMPHI- Thermoresponsive polymeric systems
15.25-15.45	Charl Faul (University of Bristol, UK) SISAM-Alignment Strategies for H-bonded and Ionically self-assembled nanostructured materials
15.45-16.05	Karen Edler (University of Bath, UK) SPENSA- Surfactant-polyelectrolytes nanostructures self-assembly
16.05-16.20	-Coffee break-

Conference Programme

Session 4: Parallel Sessions

16.20-18.00	Poster session- in display for the whole duration of the workshop (each author should be in attendance)
16.30- 18.30	Management Committee meeting SONS1/SONS2
18.00-18.30	Review Panel meeting – best poster award discussion
20.00	-Social Dinner at Maison Kammerzell Presentation of best poster awards

Friday 1 June 2007

Session 5: Devices I

Chair: **Manuel Vazquez**

9.00-9.45	Franz Himpsel (University of Wisconsin Madison, UK) Invited Lecture- Self- Assembled Nanostructures at Silicon Surfaces: From Low-Dimensional Electrons to the Limits of Data Storage'
9.45-10.05	Safia Ouazi (Ecole Polytechnique Fédérale de Lausanne, Switzerland) SANMAG- Magnetic Properties of core-shell FeCo nanostructures at surfaces
10.05-10.25	Nicolas Agrait (Universidad Autonoma de Madrid, Spain) SASMEC- Single-atom and single molecule electronic components
10.25-10.45	Dmitri D. Vvedensky (Imperial College, London, UK) SALDSOON- Step ordering in semiconductor quantum nanostructures grown on patterned substrates
10.45-11.00	-Coffee break-

Session 6: Devices II

Chair: **Jozsef Gyulai**

11.00-11.20	Franco Ciacalli (University College London, UK) SUPRAMATES- Self-Assembly of Supramolecular Materials for new Functional Structures
11.20-11.40	Saif Haque (Imperial College London, UK) SOHYD- Electron Transfer in self-organized nanostructured molecular solar cells
11.40-12.00	Christian Muller (ETH, Zurich, Switzerland) NETSOMA- Multi-component semiconducting polymer systems with low crystallization-induced percolation threshold
12.00-12.20	Anton Kiriy (Leibniz Institute for Polymer Research Dresden, Germany) NEDSPE- Nanoscale electronic devices via templating supramolecular polyelectrolytes
12.20-12.40	Nian Lin (Max-Planck Institute for Solid State Research, Stuttgart, Germany) FUN-SMARTs II- Low-dimensional supramolecular nanostructures by design
12.40-14.00	-Lunch-

Session 7: Devices III

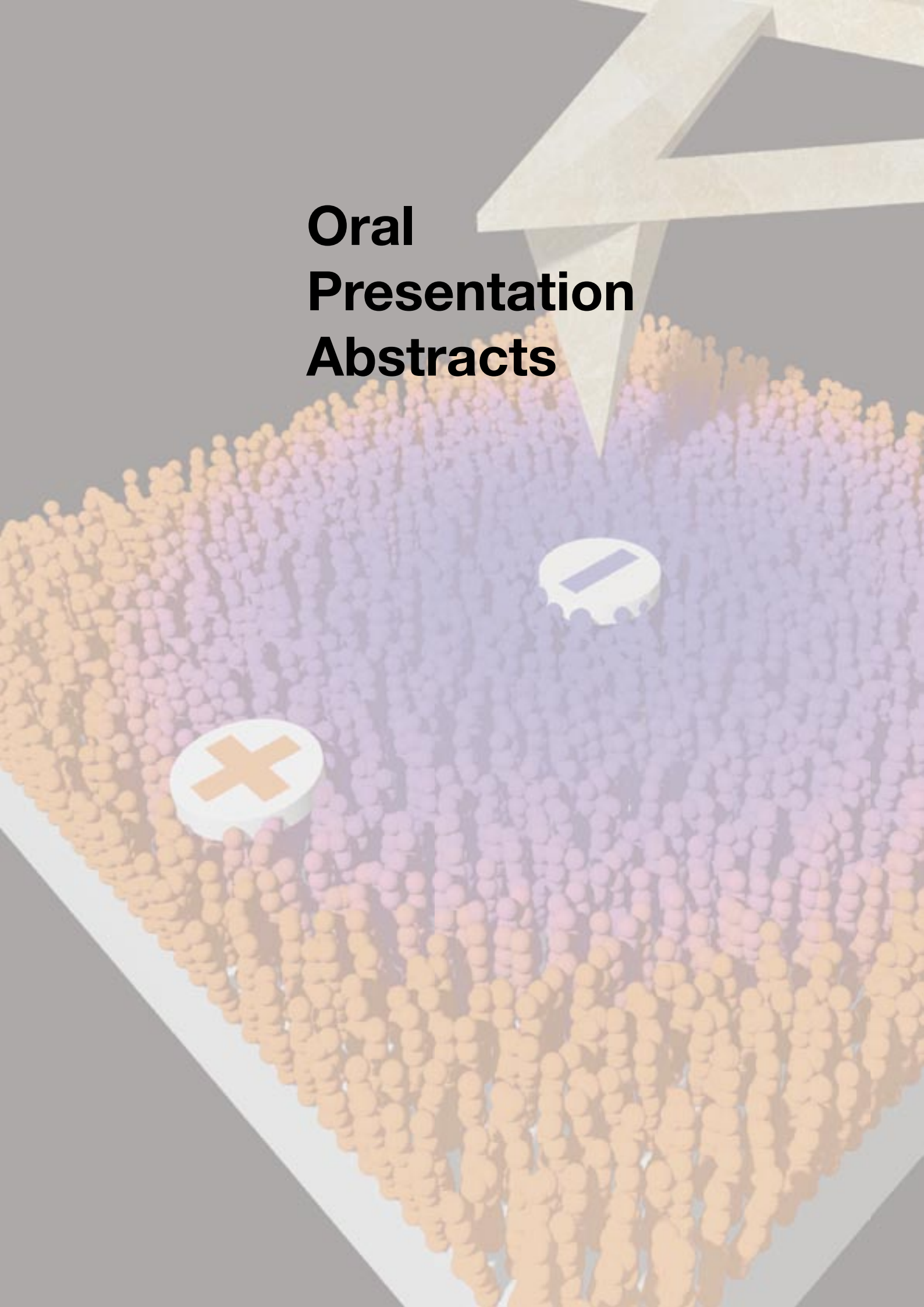
Chair: **Gareth Redmond**

14.00-14.20	Alessandro Fortunelli (IPCF, CNR, Pisa, Italy) SSA-TMN- Nucleation and growth of deposited metal nanoclusters
14.20-14.40	Dag Hanstorp (Göteborg University, Sweden) SPANAS- System for Photonic Adjustment of nanoscale aggregated structures
14.40-15.00	Jose E. Ortega (Universidad del Pais Vasco, Spain) MOL-VIC- One-dimensional supramolecular self-assembly on vicinal surfaces
15.00-15.20	Peter Reece (University of St. Andrews, UK) NOMSAN- Novel optical methods for self-assembled nanostructures
15.20-15.30	Conclusive remarks
15.30-16.00	-Coffee break-

Session 8: Parallel Sessions

16.00-17.00	Scientific Committee meeting SONS I
17.00-18.00	Scientific Committee meeting SONS II
16.00-18.00	Review Panel meeting
20.00	-Dinner- at Restaurant La Table de Christophe , Strasbourg (Invited Speakers, Scientific Committee, Management Committee, Review Panel members only)

Oral Presentation Abstracts



Oral Presentation Abstracts

Giovanni Marletta

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Invited Lecture — Self-assembling Processes at Biological Surfaces and Interfaces

Biological surfaces and interfaces have emerged as a paradigm of bottom-up processes to build up multifunctional surfaces, whose optimal organization depends exclusively on the self-organizing behavior of “smart” molecular systems. In fact, biological molecules, as peptide sequences and proteins, may play with a number of concurrent effects, like the simultaneous presence of hydrophobic, electrostatic and hydrogen bonding, to switch on very effective and highly specific 2D and 3D self-assembling/self-organizing behavior.

In the present lecture the attention will be focused on the interplay among properties of biological systems and the surface/interface properties. In particular, the self-assembly processes yielding variously shaped bidimensional domains like stripes, fibers and dots, will be discussed in view of the molecular structure of the employed compounds and the substrate composition and properties including surface free energy, electrical properties and surface morphology.

Case studies involving the formation of ordered structures with proteins, oligopeptides, and phospholipids onto inorganic and polymeric surfaces will be discussed, with a special focus onto self-organizing peptides, which promise to be the ideal building blocks to produce ordered and dynamically stimulus-responsive structures. Thus, a special focus will be dedicated to the behavior of new synthetic helical peptides as well as ionic self-complementary peptides on surfaces. This latter class of peptides, in particular, shows unique structural features involving the simultaneous presence in the same molecule of hydrophilic and hydrophobic molecular surfaces as well as regular repeats of positively and negatively charged amino acid residues on the hydrophilic surface of the molecule.

The perspective of the employed techniques in the context of the developing patterning technologies will be discussed.

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BIONICS— The Programmed Self-assembly of DNA as a Tool for Controlling the Structure and Function of Matter on the Nanoscale

The base pairing code between oligonucleotides is probably the most flexible and usable code that a chemist can exploit to organize the specific interaction between an arbitrary number of macromolecules. The current structural knowledge on DNA also makes this code a geometric one, as the shape of an assembled object can be predicted. Taking advantage of this, and of the possibility to obtain oligonucleotides of practically any sequence and length (especially thanks to solid-state synthesis), a great variety of DNA nanostructures can be prepared from a mix of oligonucleotides of properly designed base sequences [1].

One of the most interesting structural motifs of use in this context is the four-way junction: a branched form of DNA that can be used as the structural element for building a plethora of building blocks and, using them, nanostructures. Many examples have been presented in the literature about 1D, 2D and even 3D nano-objects prepared by the self-assembly of branched DNA.

By connecting 4 four-way junctions, we can prepare mechanically-rigid parallelogram-shaped DNA building blocks that can be used as such to control the spacing and orientation of other nano-objects in space (organic moieties or proteins, for example) that can thus be brought together in a hybrid supramolecular nanostructure. Alternatively (or additionally), the DNA parallelogram building blocks can be polymerized supramolecularly to give more complex nanostructures containing different hierarchical levels of interactions. Rigid linear, branched or even two-dimensional arrays can be prepared [2]. The size of the obtained nanostructures can be extended to the micrometer range by assembling the oligonucleotides on longer "carrier" single-stranded DNA molecules. The assembly of the nano-structures can be characterized by gel electrophoresis and atomic force microscopy.

The conformational polymorphism of DNA, or the possibility of isothermally substituting specific strands in nanostructures can be exploited to controllably change the shape of a nano-object. So, it is possible to make switches, logic gates, nanomotors or similar devices that can react mechanically to an external stimulus, chemical or physical in nature. We have designed, prepared and characterized a DNA nano-switch based on a duplex-triplex transition that can respond to pH changes in the solution and bring together or set apart some organic moieties that are located on the termini of oligonucleotides [3]. The switching of the device has also been characterized by single-molecule fluorescence.

[1] Brucale M, Zuccheri G, Samori B "Mastering the complexity of DNA nanostructures" *Trends in Biotechnology*, 2006, 24: 235-243.

[2] Brucale M, Zuccheri G, Rossi L, et al. "Characterization and modulation of the hierarchical self-assembly of nanostructured DNA tiles into supramolecular polymers" *Org Biomol Chem* 2006, 4: 3427-3434.

[3] M. Brucale, G. Zuccheri, B. Samori, "The dynamic properties of an intramolecular transition from DNA duplex to cytosine-thymine motif triplex" *Org Biomol Chem* 2005, 3, 575.

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BIOSONS — Purpose and adaptability: induced self-assembly of a biological peptide motif

Cells as functional units from algae to mammals demonstrate the most remarkable degree of self organisation. Processes like membrane formation, protein folding and signal cascades excel in selectivity and control. Nanotechnology is often inspired by biological properties but, despite nature's seductive elegance and putative simplicity, often fails at prediction of complex self-assembly. Even weak forces, multiplied by the large number of subunits, contribute to the assemblies and frequently lead to unforeseen results.

There is a rising interest in vesicular self-assemblies to exploit the functionality of such separated compartments, and the number of potential applications increased with complexity of the membrane material. Controlled variation of structure and dimension in supramolecular assemblies is a desirable feature for medical and technical applications. From lipids to polymers to the incorporation of proteins: today we are able to tailor membrane properties desirable for many purposes.

Even though the biological function of proteins and peptides must be considered exemplar for the discipline of self-assembly, it is a challenge to control their intermolecular interactions apart from their biological task. Membrane formation of short peptides (< 30 AA) is difficult to establish mainly due to the hydrophilic contribution of every single amino acid's backbone.

In this work we present a novel material inspired by nature, surprising both in its specificity of self-organization and abstraction from its biological purpose. The peptide's general secondary structure was characterized earlier by X-ray crystallography studies and acts as a suitable hydrophobic constituent when it comes to the formation of an entirely peptidic membrane. We complemented its native hydrophobic structure with hydrophilic lysine sequences to obtain purely peptidic amphiphiles, unique in their property of controlled self-assembly.

We investigated the influence of varying lysine chain lengths on the assembled structures and characterized them by TEM, SEM, AFM, light scattering as well as circular dichroism measurements.

Duncan S. Sutherland

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NANO-SMAP — Utilising colloidal templates to nanopattern macromolecules over large areas for biological applications

The recent decade has seen a vast expansion in the ability to create and study nanometer scale objects. These new technologies are increasingly being applied to develop understanding of biological systems. Both water and electrolyte ions play a critical role in living systems and an important part of nanoscale engineering for life science is the ability to define and study systems in relevant environments. The immobilization of bioactive macromolecules, such as proteins at interfaces has long been a goal in biosensing, biomaterials, tissue-engineering research and for use as detection systems, stimulatory cues for biosystems or as simplified model systems to study biointeractions. With the advent of soft lithographies and efficient approaches to minimise non-specific protein binding at interfaces (by for example presentation of dense oligo polyethylene glycol surfaces) microscale patterns of proteins were successfully realised and applied as model systems with significant impact on the study of biological systems. While patterns at the micrometer scale are of considerable interest and application, the size of, and length scale at which proteins and other macromolecules are structured is in most cases at the nanoscale. Patterning biomolecules at the nanometer scale gives a significant potential for studying how biological systems function at the macromolecular length scale or to mimic the structure of biological interfaces with macromolecular resolution. Approaches to the large area patterning of proteins and other macromolecules based on colloidal templates will be described. Inorganic templates of $\text{SiO}_2/\text{TiO}_2$ or SiO_2/Au generated by electrostatically assembled colloidal particle masks [1] and traditional lithography have been used to assemble first PEG containing copolymers [2] then nanopattern proteins over large areas [3,4]. Alternative approaches have utilised sacrificial colloidal masks [5]. Nanopatterned PEG containing layers and protein arrays have been used to study cellular adhesion and differentiation.

[1] P. Hanarp, D.S. Sutherland, J. Gold and B. Kasemo «Control of nanoparticle film structure for colloidal lithography» *Colloids and Surfaces A* 214: 23-36 (2003)

[2] M. Gnauck, E. Jaehne, T. Blaettler, S. Tosatti, M. Textor and HJP Adler „ Carboxy-terminated oligo(ethylene glycol)-alkane phosphate: Synthesis and self assembly on titanium oxide surfaces” *Langmuir* 23 (2):377-381 (2007)

[3] H. Agheli, J. Malmstrom, P. Hanarp and D.S. Sutherland “Nanostructured biointerfaces” *Materials science and engineering C Biomimetic and supramolecular systems* 26 (5-7): 911-917 (2006)

[4] H. Agheli, J. Malmstrom, E.M. Larsson, M. Textor and D.S. Sutherland “Large area protein patterning for biological applications” *Nano Letters* 6 (6): 1165-1171 (2006)

[5] J. Vörös, T. Blättler, M. Textor, “Bioactive Patterns at the 100-nm Scale Produced Using Multifunctional Physisorbed Monolayers”, *MRS Bulletin* 30(2): 202-206 (2005)

Prof. John E. Anthony

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Invited Lecture — Tuning aromatic π - π interactions for improved film morphology and device performance

The field of organic electronics would not exist without the unique ability of organic molecules to self assemble. This assembly process is driven by numerous electrostatic and steric influences, and can be directed by chromophore functionalization using well-established synthetic techniques. The wealth of process that direct intermolecular interactions allow the synthetic chemist to select the strength with which the molecules interact, directing the materials to form large crystals or disperse films on surfaces. This ability of nanometer-sized molecules to spontaneously assemble into highly-ordered structures many microns in size highlights the advantage to using organic molecules in electronic applications.

The use of several driving forces for self-assembly will be discussed. Perhaps the simplest approach is to tailor the shape of a molecule to exploit π -stacking interactions so prevalent in biological self-assembly. Appropriate substitution in this fashion leads to a dominant π -stacking motif, that can be exploited by directed crystallization to yield crystalline ribbons on surfaces in widths from 1 – 50 μm . The π -stacking axis of these crystals is almost perfectly aligned with the long axes of the crystals, allowing detailed study of the anisotropy of transport properties in these materials. Further changes in the steric environment around the aromatic chromophore can be used to tune the dimensionality of π -stacking interactions; as the packing motif changes from 2-dimensional π -stacked arrays to predominantly 1-dimensional π -stacking interactions, significant changes in the hole transport in thin-film devices can be observed. Changes as small as 0.25 Å in the separation between adjacent π -stacks can lead to a decrease in hole mobility of more than two orders of magnitude.

Further tuning of supramolecular order can be achieved by introducing electrostatic interactions. The addition of strongly electron-withdrawing groups (e.g. fluorine) to an aromatic periphery allows closer contact of the aromatic planes, resulting in improvements in transport properties. Secondary tuning of aromatic self-assembly driven by fluorine-fluorine or fluorine-sulfur interactions can dramatically alter the morphology of films arising from solubilized aromatic chromophores. The exploitation of relatively weak F---S interactions allows subtle tuning of intermolecular overlap, and slow formation of crystals yielding highly uniform thin films. These two factors combined yield impressive improvements in transport properties, along with the ability to control nucleation in the growing film by proper treatment of the substrate. Alternatively, exploitation of stronger F---F interactions leads to fast crystallization, leading to the growth of very large (up to several cm on a side) crystals with smooth surfaces suitable for use as substrates for single-crystal device fabrication. The ability to control the bulk morphology of organic semiconductors is critical to the technological applications of these materials. The use of aromatic self-assembly process to control this parameter allows for the minute tuning of both intermolecular interactions and resulting film aspect, providing a straightforward avenue for improvements in device performance.

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FunSMARTs I — Supramolecular engineering with linear dicyanitrile molecules on Ag(111): 2D-chiral kagomé lattice and tuneable nanoporous metal-organic networks

Molecular self-assembly on surfaces offers the possibility to design new low-dimensional organic and metallosupramolecular architectures. Here we present a systematic scanning tunnelling microscopy study of the self-organized growth of linear polyphenyl-dicarbonitrile molecules on Ag(111). Although all molecules have the same functional endgroups, and only differ in the number of phenyl rings ($n = 3, 4, 5$ with corresponding length of 1.6 nm, 2.1 nm, and 2.5 nm, respectively), completely different organic networks evolve. The formed topologies range from densely packed parquet like patterns to the open and complex arrangement of a hitherto unobserved 2D-chiral kagomé lattice realized with the pentaphenyl species (see Fig. 1a).

When the cyano moieties are employed for Co-directed assembly of metal-organic coordination networks, a threefold coordination motif is encountered for all linkers. The self-organization of the honeycomb networks is essentially determined by the two dimensionality of the crystal surface and the metal-ligand interactions (see Fig. 1b). Highly ordered networks of hexagonal nanocavities can be built extending over micrometer large areas as single domains with a low defect concentration. The size of the cavities is controlled by the number of phenyl rings in the molecules, whereby the provided open spaces can be used to confine guest molecules and study 2D rotations.

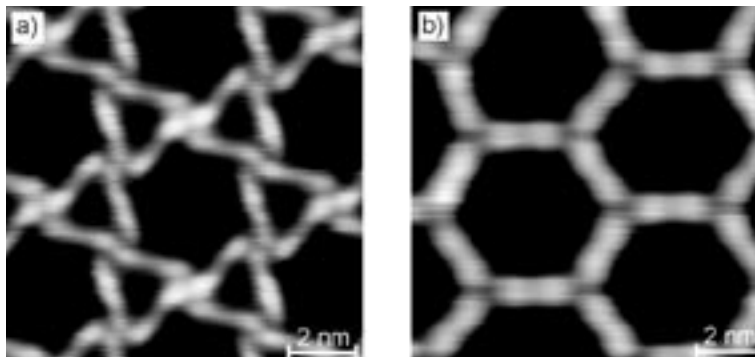


Fig. 1: STM data of network topologies achieved with pentaphenyl-dicarbonitrile molecules on Ag(111). a) Chiral organic kagomé lattice formed by the self-assembly of the pure molecules. b) Co-directed assembly of a metal-organic network with a threefold coordination motif, defining open spaces with 5.5 nm in diameter.

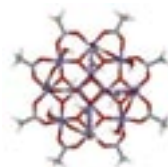
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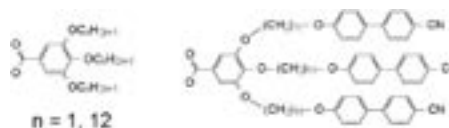
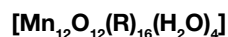
LC-NANOP — Liquid crystalline self-organization of $[\text{Mn}_{12}\text{O}_{12}(\text{RCO}_2)_{16}(\text{H}_2\text{O})_4]$ clusters derivatives

The aim of molecular electronics is to use molecules as active entities in electronic devices with the basic idea that one (or several) molecule could achieve the same task as a classical electronic component. The principal advantage of such a “bottom-up” approach is mainly the miniaturization aspect. Many efforts of development were carried out during the last ten years, mainly in the field of information storage. The major breakthrough in this domain was the discovery of single molecular magnets (SMMs) in the early eighties. A few derivatives of the cluster $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4]$ (Scheme 1) were then synthesized but with poor results in term of organization so far, precluding any efficient addressing of the molecules. One way to organize a molecular entity is the control of the intermolecular interactions. This approach is very often used in the field of liquid crystals. The micro-segregation which is the first step of the self-organization is strongly dependent on the molecular interfaces and shapes.



Scheme 1 : Cluster $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$

We have therefore designed several derivatives of $[\text{Mn}_{12}\text{O}_{12}(\text{R})_{16}(\text{H}_2\text{O})_4]$ in which the various peripheral groups (R) have been systematically modified to give various molecular geometries and interfaces compatible with liquid crystals constraints (Scheme 2).



Scheme 2 : Derivatives of $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$

The compounds were fully characterized and found to exhibit interesting liquid crystalline properties. Furthermore, it was shown that the original magnetic behaviour of $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ was preserved. These results will be presented and discussed.

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SCALES — Complexity across length scales in soft matter

Recent collaborative work has shown that low-molecular weight T-shaped ternary amphiphiles consisting of aromatic rods, with flexible hydrophilic and lipophilic groups attached, can self organize to a series of unexpected new liquid crystalline phases with 1-, 2- and 3-d periodicity.[1] Most prominent among them are honeycomb structures with aromatic walls surrounding either polar or non-polar channels of different polygonal cross-sections and combinations of columns and layers. Among the polygonal cylinder structures, there are also cylinders which have a pentagonal shape and uniform periodic structures composed of cylinders with a different shape. These structures are closely related or even more complex than those found in multiblock copolymers. However the block copolymer structures are nearly an order of magnitude larger. More generally, soft matter has the ability to self-organize on different length scales: periodic 1-, 2- and 3-d arrays occur in lyotropic and thermotropic liquid crystals (1-10 nm), di- and triblock copolymers (10-100 nm) and in colloidal systems (0.1-1 μm). The target of this project is to increase the complexity of the self assembled structures by increasing the number of incompatible components, and to cross the length scales from complex self-organized liquid crystalline mesophases of well designed low molecular weight amphiphiles to the complex morphologies formed by multiblock copolymers.

In this contribution, recent progress in the design of complex LC structures will be summarized and the general importance of the results for materials design at different length scales and in different systems (crystal engineering, block copolymers, etc.) will be outlined. Based on this, the targets of the SCALES project will be explained and the first results presented.

[1] B. Chen, X. Zeng, U. Baumeister, G. Ungar, C. Tschierske, *Science* **2005**, 307, 96-99.

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Invited Lecture — Molecular Recognition in Chemomechanical Polymers

Molecular recognition is the basis of most biological functions, including the control of motions, vessel changes etc. New technologies use molecular recognition with synthetic host systems as basis for many applications. We will discuss how supramolecular complexes can be used as basis for new intelligent materials, such as artificial muscles/actuators, or as new drug delivery devices. The implementation of supramolecular binding sites into flexible polymers allows to translate **selective** molecular recognition events into large macroscopic motions. Uptake of effector compounds from the aqueous surrounding can lead to fully reversible size expansions of such polymer films by up to 2000% in volume, or to contractions of similar size.

Most of our hydrogels contain e.g. polyamines and lipophilic alkyl or aryl groups as host components, and show different expansions for a large variety of effectors. Most recently it has been shown, how such polymers can be used to release selectively drugs such as insulin as function of **glucose levels** in blood plasma. The dimension changes can dramatically depend on the presence or **two** effector compounds in the surrounding medium, either with negative or with positive cooperativity. The macroscopic dimension change occurs if two different effectors are present within a narrow concentration range, thus providing for the first time a chemically induced macroscopic logical AND gate. Selective interactions of the covalently attached supramolecular polyamine binding sites with transition metal ions have been shown to lead to dramatic macroscopic size changes by simultaneously added metal chelators, aminoacids and peptides. With chitosan-derived gels we have been able to translate for the first time **chiral recognition** into directly measurable macroscopic motions. An important, until now often overlooked possibility to enhance the sensitivity of the actuator volume changes is the downsizing of the polymer particles. Miniaturization of chemomechanical polymer particles holds much promise for both enhanced response sensitivity and velocity.

Selected papers from the Saarbrücken group:

- «Molecular Recognition in a Supramolecular Polymer System Translated into Mechanical Motion» *Angew. Chem. Int. Ed. Engl.* **2003**, 42, 3544-3546.
- «Large macroscopic size changes in chemomechanical polymers with binding sites for metal ions» *Chem. Commun.* **2004**, 100-101.
- «Molecular Recognition in a Supramolecular Polymer System Translated into Mechanical Motion» *Angew. Chem. Int. Ed. Engl.* **2003**, 42, 3544-3546.
- «Large macroscopic size changes in chemomechanical polymers with binding sites for metal ions» *Chem. Commun.* **2004**, 100-101.
- “Sensitivity increase in molecular recognition by decrease of the sensing particle size and by increase of the receptor binding site – A case with chemomechanical polymers” *Chem. Commun.* **2004**, 2436 to 2437.
- „Ternary Complexes for Large Motions of a Chemomechanical Polymer Induced by Metal Chelators, Aminoacids and Peptides” *Tetrahedron Lett.* **2005**, 46, 751-754.
- “A chitosan-based chemomechanical polymer triggered by stacking effects with aromatic effectors including aminoacid derivatives” *Tetrahedron* **2005**, 61/36, 8694-8698.
- “Dimension Changes in a Chemomechanical Polymer Containing Ethylenediamine and Alkyl Functions as Selective Recognition Units” *Eur. J. Org. Chem* **2006**, 677–692.
- “A Chemomechanical Polymer that Functions in Blood Plasma with High Glucose Selectivity” (with R Strongin et al) *Angew. Chem. Int. Ed.* **2006**, 45, 5319–5322.
- “Chemomechanical Polymers” In: „Intelligent Materials, M.Shahinpoor and H.-J.Schneider, Ed. Royal Soc.Chem., Cambridge UK, **2007**.
- “The direct translation of chiral recognition into mechanical motion” *Angew. Chem. Int. Ed.* **2007**.

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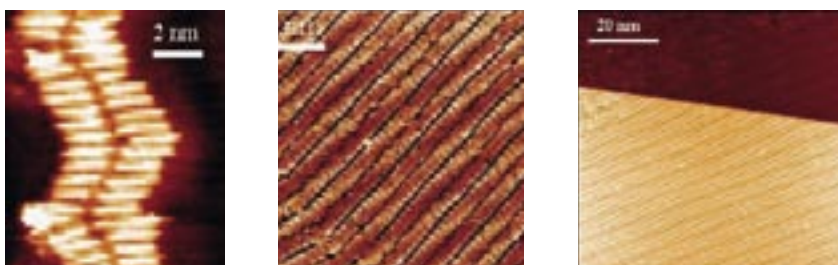
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SONS-AMPHI — Long time evolution of order on a hierarchy of length scales in self-organized monolayers of supramolecular polymers

The process of self assembly at multiple length scales is studied by low temperature scanning tunnelling microscopy for bis-urea substituted toluene deposited on Au(111) surfaces by evaporation under high vacuum. The design of the molecules at the supramolecular chemistry level (hydrogen bonds can be formed at specific sites) allows for the formation of long polymeric chains as observed in solution. However, bringing these molecules to surfaces in vacuum, also less strong interactions become highly relevant and impose an unexpectedly important influence on the two-dimensional organisation of these molecules, leading to the formation of hierarchically structured patterns covering length scales from the molecular building units up to perfectly organized supramolecular assemblies of areas larger than some 10^4nm^2 (F. Vonau *et al.*, *Phys. Rev. Lett.* **94**, 066103 (2005)). Due to the electronic properties and the particular conformation of these molecules, a tunnel transparency allows us to detect simultaneously both the supramolecular layer and the gold surface underneath. As the Au(111) surface reconstruction defines a specific crystallographic direction, it is possible to follow the interlocking of the supra-molecular layer with the substrate as a function of surface coverage and annealing time (from several months up to one year under UHV conditions at room temperature). Our results demonstrate the interplay between molecule-molecule and comparatively weaker molecule-substrate interactions. The latter are becoming less influential as the size of the perfectly organized, crystalline domains (and thus the number of coherently interacting molecules) increases with annealing time. This quasi-decoupling from the substrate is nicely demonstrated by the observation that a large 2D-layer of perfectly ordered supramolecular polymers (obtained after long maturation time) is able to cross over monoatomic steps in the substrate without perturbation of its 2D structure. We present a possible mechanism for explaining the change in interlocking with the substrate by a cooperative process which involves a large number of supramolecular polymers. We also show a mechanism characteristic for the self-assembly of supramolecular polymers and impossible for covalently formed polymers.



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AMPHI — Thermoresponsive polymeric systems

We have investigated two types of polymeric systems – thermoresponsive nanoparticles and thermoresponsive microemulsion networks.

1. Properties of nanoparticles of poly(*N*-isopropylacrylamide) [PNIPA] stabilised by surfactants were investigated in solutions in the phase separated region above LCST. The presence of a surfactant induces formation of well-defined thermoresponsive nanoparticles in the size range 20 to 120 nm. The stabilization can be qualitatively explained by interaction of monodisperse nuclei of PNIPA with surfactants in the transition region of phase separation of PNIPA solutions.
2. When an inversely selective diblock copolymer is added to a mixture of two immiscible solvents, microemulsion particles are created with diameter approximately 50 nm that containing the minority solvent. At higher concentrations, the system can self-organize into a three dimensional network of microemulsion nanoparticles encapsulating the minority solvent in the majority matrix. If the two solvents exhibit a coexistence curve in the phase diagram, the structure can be reversibly destroyed by heating above the phase transition. Such a system can be realized, e.g., in a mixture of partially miscible solvent heptane/dimethylformamide ($T_c = 75^\circ\text{C}$) and a diblock copolymer of octylstyrene-*b*-butylmethacrylate. Various examples of such microemulsion networks will be discussed.

We acknowledge support by the Grant Agency of the Czech Republic (SON/06/E005) within the EUROCORES Programme SONS of the European Science Foundation, which is also supported by the European Commission, Sixth Framework Programme.

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SISAM — Alignment strategies for H-bonded and Ionically Self-Assembled Nanostructured Materials

Building ordered two- and three-dimensional nanostructures in a facile way is essential for the next generation of electrical, optical and magnetic materials and devices. Molecular self-assembly is a versatile method to prepare such structures. However, to ensure that structure formation is not only local, alignment of such multi-domain materials is essential.

Strategies applied on both ionic as well as hydrogen-bonded systems include oscillatory shear, steady-state shear as well as photo-alignment. Oscillatory shear, which is a commonly used technique for aligning block-copolymer systems, did not show good reproducibility for the macroscopic alignment of the ionic systems. The use of steady-state shear, however, showed to be promising to obtain uniformly anisotropic samples. New insights into the alignment process and factors affecting the order of perylene-surfactant based system using a steady-state shear approach are discussed.

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SPENSA — Surfactant-PolyElectrolyte Nanostructure Self-Assembly

The project SPENSA has been generally concerned with the interaction of polyelectrolytes with interfaces. Our primary work has concentrated on developing an understanding of a novel film-forming polyelectrolyte-surfactant system, which was to have been linked with theoretical work, and investigations of biological polyelectrolytes at interfaces, however due to lack of funding, the latter part of this work has not progressed. Investigations of the polyelectrolyte-surfactant membranes has proved to be highly interesting, has given rise to new collaborations and further funding for development towards applications. We will describe our studies of these films in this presentation.

It is well known that certain polymers in surfactants will interact in solution, which, due to the surface activity of the surfactant (and sometimes the polymer as well) will generally form a thin (around 10 nm) film at the air/water interface. However, we have found that certain combinations of polymers and surfactants will form much thicker (up to 100 micron) and more organized films. These films are self-supporting and assemble through interactions between water-soluble neutral polymers with polarisable groups, and surfactant micelles or vesicles having a well defined range of surface charge. They form spontaneously at the surface of homogeneous solutions containing both the polyelectrolyte and surfactant and contain a highly ordered array of micelles. The films form across the entire open area of the container in which they form, allowing production of arbitrarily large areas of the membrane which can be lifted from the solution surface after cross-linking onto either solid substrates or as membranes on an open mesh. This opens up a number of potential applications such as the slow release of hydrophobic drugs incorporated in the surfactant micelles present in the mesostructured polymer film.

We have studied the formation of these membranes using a range of techniques including Brewster angle microscopy, small angle X-ray and neutron scattering, X-ray and neutron reflectivity and surface tension to probe both the film at the solution surface and the properties of the subphase solution. We will report on our investigations on the formation processes involved in the formation of these membranes, and our initial attempts to exploit these films through encapsulating hydrophobic species into the ordered micelle array within the films. We have also successfully expanded the range of film-forming systems from the polyethylenimine-cetyltrimethylammonium bromide solutions where we first observed film formation, to mixed cationic surfactant solutions which form films with many water soluble polymers.

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**Invited Lecture — Self-assembled Nanostructures at Silicon Surfaces:
From Low-Dimensional Electrons to the Limits of Data Storage**

This talk has three themes:

1. Fabricate atomically-precise nanostructures at surfaces, particularly nanowires consisting of atom chains.
2. Explore the behavior of one-dimensional electrons in atom chains.
3. Find the fundamental limits of data storage using an atomic scale memory.

Semiconductor surfaces lend themselves towards self-assembly, because the broken bonds create elaborate reconstruction patterns to minimize the surface energy. Also, the surface electrons near the Fermi level completely de-couple from the substrate, because their energy lies in the band gap. Angle-resolved photoemission reveals surprising features, such as a fractional band filling and a spin-splitting at a non-magnetic surface. An interesting by-product is an atomic scale memory, which stores a bit by the presence or absence of a single silicon atom. This toy memory is used to test the fundamental limits of data storage and to make a comparison with hard disks and DNA.

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SANMAG — Magnetic properties of core-shell FeCo nanostructures at surfaces

The magnetic energy of a ferromagnetic nanosystem depends on the direction of its magnetization. Some preferential orientations are stable if the energy barrier – related to the anisotropy energy – is high enough as compared to thermal fluctuations. Thus for a system composed of 1000 atoms, the blocked regime at room temperature requires an anisotropy energy of 0.5 to 1 meV per atom. In nanostructures, the reduced size, the high number of low coordinated atoms and the possibility to grow metastable strained structures can lead to enhanced anisotropy energy. For example, a single deposited Co atom on Pt(111) has an anisotropy of 9 meV [1]. Recent theoretical prediction and experiments on thin films suggest that bimetallic nanoislands composed of Fe and Co should present high anisotropy.

We present here the first study of the magnetic properties of deposited bimetallic nanostructures by controlling the structure. We combined in-situ magneto-optical Kerr effect measurements (MOKE) and scanning tunneling microscope (STM) measurements on bimetallic FeCo nanostructures on Pt(111). The blocking temperature (T_B) depends on the alloy composition: in Fe_{0.5}Co_{0.5}, it is 200 percent enhanced as compared to pure Fe or Co. We studied separately the influence of the Fe-Co interface existence on T_B . We discuss the link between T_B and the island anisotropy energy.

[1] P. Gambardella et al., Science **300**, 1130 (2003)

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SASMEC — Single-Atom and Single-Molecule Electronic Components

The objectives of our project were to answer some fundamental questions related to transport through atomic chains and single-molecule junctions, both experimentally and theoretically. Our experiments have been conducted mainly at low temperatures using scanning tunneling microscopes (STM) and mechanically controllable break junctions (MCBJ). The atomic chains were characterized using conductance measurements (I-z curves, dI/dV spectroscopy) and force measurements. We have made good progress in understanding the structure, stability, formation dynamics, dissipation, and coupling of mechanical and electrical properties in atomic chains of gold and platinum, as well as the influence of adsorbates and formation of hybrid chains.

Similar techniques were used to study the conductance of single molecules. We have concentrated on simple molecules, like H₂, S, CO, O₂, Benzene, in a well controlled experimental situation in order to insure that contact is established with a single molecule. We have tried to obtain as many experimental parameters as possible in order to have a well-defined system for comparison with calculations. The parameters included the conductance, the number of conductance channels (using conductance fluctuations, shot noise or superconducting subgap structure), the vibration modes (using dI/dV spectroscopy), stretching dependence of the vibration modes, and variation with isotope substitutions, and the force constant of the junction. The added advantage of using simple molecules is that they can be handled well in numerical simulations. The simple molecules provide benchmarks against which the theoretical approaches can be tested.

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SALDSON — Step-Ordering in Semiconductor Quantum Nanostructures Grown on Patterned Substrates

High-quality III-V semiconductor quantum wells (QWs) with narrow photoluminescence (PL) linewidths and high electron mobilities are central to fundamental studies and a number of device applications. The optical and electrical transport properties of such QWs and other semiconductor nanostructures are determined by the extent of impurity incorporation and the quality of their interfaces. Although III-V QWs are typically produced by molecular-beam epitaxy, growth by metallorganic vapor-phase epitaxy (MOVPE) provides an attractive alternative in view of its advantages in a production setting and the possibility for making novel quantum wire and quantum dot structures.

In this talk we will describe recent experiments and an accompanying theory for the growth of GaAs/AlGaAs QWs produced by MOVPE on slightly misoriented substrates. The small misorientation is sufficient to modify the growth mode and surface morphology of the epilayers, which has a significant effect on the optical and transport properties. Measurements have revealed low-temperature PL linewidths as low as 0.6-meV and low-temperature electron mobilities greater than $10^6\text{cm}^2/\text{Vs}$ in GaAs/AlGaAs QWs produced by MOVPE on slightly misoriented substrates [1].

We have developed a model that accounts for the surface morphologies seen by in these experiments, ranging from nucleation and growth of islands on terraces to different types of step bunching. Our model is based on the following schematic MOVPE sequence. TMGa and AsH₃ arrive at the substrate by diffusion through a boundary layer, after which these species and any of their fragments migrate with minimal lateral interactions to step edges, where they release Ga and As through decomposition reactions. The highly mobile surface species can lead to step-flow growth with terrace lengths of up to several microns, which prevents the direct simulation of this scenario, but presents no problem to a formulation in terms of our (one-dimensional) Burton-Cabrera-Franck (BCF) type equations. The model includes only the most basic kinetic steps, but is nevertheless able to reproduce quantitatively the trends in the morphology observed in experiments.

The observation of step ordering on patterned, slightly misoriented substrates and its interpretation using kinetic Monte Carlo simulations will [2] also be discussed.

[1] E. Pelucchi *et al.*, J. Appl. Phys. **99**, 093515 (2006).

[2] A. Da Volta *et al.*, Appl. Phys. Lett. **88**, 203104 (2006).

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SUPRAMATES — Self-Assembly of SUPRAMolecular MATerials for new functional StructurES

I will present our recent approaches to design, synthesis, fabrication, characterisation and exploitation of organic semiconductors nanostructures and nano-objects as a way of introduction to the project SUPRAMATES, that has recently started in the context of the SONS2 initiative.

I will begin this presentation with an introduction to the activities carried out at University College London (Physics Department and London Centre for Nanotechnology) that include both characterisation of the optical and electrical properties of self-assembled threaded molecular wires¹, and on near-field optical microscopy and lithography of organic semiconductors nanostructures².

The second part of my talk will focus on the overall objectives of SUPRAMATES and in particular on how well-known and newly-designed functional self-assembling building blocks with extended pi-conjugation³⁻⁵ or high persistence length⁶ will be manipulated⁷ to yield supramolecular functional architectures, incorporated into large area and single-nanoobject device structures⁸, to be later investigated both in terms of their fundamental optical and electronic properties, and, where appropriate, explored for their applicative potential.

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Oral Presentation Abstracts

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SOHYD — Electron transfer in self-organized nanostructured molecular solar cells

Organic electronic devices such as organic photovoltaics (OPV) and light emitting diodes (LEDs) are built by electrically integrating molecular components at the sub-micron level. It is now widely accepted that a key challenge for the development and subsequent optimization of such devices is the ability to control materials structure at the nanometer length scale. In the case of organic solar cells the nanomorphology of the donor-acceptor layer can have a significant impact upon the interfacial electron transfer dynamics. For example, in order to achieve efficient charge separation it is essential to structure the active morphology on the materials exciton diffusion length. In addition, charge transport through the domains needs to be enhanced in order to minimize charge recombination losses. A general approach to improve charge transport is to increase the mesoscopic order at the nanometer-level. In this talk we will pay attention to the use of supramolecular chemistry / molecular self-assembly strategies to achieve control of materials structure at the nanometer length-scale in order to modulate interfacial dynamics and achieve a more efficient device performance. More specifically, we will focus on our recent time-resolved spectroscopic studies of charge separation and recombination in self organized donor-acceptor block copolymers. We will present systematic studies of interfacial electron transfer as a function of nanomaterials structure. These investigations are undertaken with the intention of developing predictive, quantitative structure-function relationships (establishing design principles and materials engineering rules), which are capable of being employed to guide optimization and development of efficient photovoltaic devices.

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NETSOMA — Multi-component semiconducting polymer systems with low crystallization-induced percolation threshold

In various applications of polymers, blends and other multi-component systems are employed in order to meet multiple requirements which cannot be fulfilled by a single material. For instance, in polymer optoelectronic devices it is often highly desirable to combine the semiconducting properties of the conjugated species with the excellent mechanical properties of certain commodity polymers. To this end, so far, most efforts on bi-component systems have concentrated on use of amorphous-amorphous and amorphous-crystalline materials combinations, whereas exploration of *crystalline-crystalline* binaries have been relatively rare. This is rather surprising as the crystalline nature of the components may provide a significantly broader range of means to control the microstructure and, hence, properties of the final object when compared to systems comprising amorphous species. Here we investigate bi-component blends and diblock copolymers comprising semicrystalline regio-regular poly(3-hexyl thiophene) (P3HT) and selected semicrystalline commodity polymers, and show that due to a highly favorable, crystallization-induced phase segregation of the two components, during which here the semiconductor is predominantly expelled to the surfaces of cast films, vertically stratified structures can be obtained in a one-step process. Incorporating the latter as active layers in polymer field-effect transistors (FETs), we find that the concentration of the semiconductor can be reduced to values as low as 3 wt% without any degradation in device performance. This is in stark contrast to conjugated polymer systems comprising an amorphous insulating polymer, for which significant reduction in electrical performance was reported. Crystalline-crystalline/semiconducting-insulating multi-component systems offer an expanded flexibility for realizing high-performance semiconducting architectures at drastically reduced materials cost and with, among other things, enhanced mechanical properties and improved environmental stability without the need to design all performance requirements into the active semiconducting polymer itself.

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NEDSPE — Nanoscale electronic devices via templating supramolecular polyelectrolytes

We are going to report our results obtained during the work in the frame of NEDSPE project. In general, the project aimed to develop methods of the fabrication and positioning/addressing of supramolecular objects composed from metallic clusters, electroconductive and dielectric polymers. The main tasks formulated in the proposal were solved and even a number of unexpected results were obtained. In particular, we developed general methods to handle single polyelectrolyte molecules: immobilization on various surfaces in desired conformations, imaging, manipulation, deposition of some desired materials (both inorganic and organic) selectively along polyelectrolyte molecules. Method to (semi)conductive polypyrrole (Ppy) nanofibers produced through polymerization from individual polyanion molecules was developed. We demonstrated that they are electrically conductive and that the conductivity indeed comes from single fibers. These achievements are a basis for construction of simplest devices. Several useful analytical methods were developed, such as i) a contrasting procedure allowing visualization of single molecules even on relatively rough surfaces and ii) direct measurement of molecular contour length and molecular weight distribution of polyelectrolytes using AFM. We also reported modification of multiwalled carbon nanotubes with polymer brushes that made them easily dispersible in water and gave a possibility of further modifications of their surfaces on a desired fashion. Finally, we employed the dispersion of P2VP-modified CNTs for a preparation of thin coatings which appeared to be highly conductive and moderately transparent.

Very recently we developed method to deposit large arrays of of stretched and aligned synthetic PE molecules in a shear flow gradient, derived by a receding meniscus. For this, a drop of PE solution was deposited with the aid of a pipette onto PDMS film (such as, PDMS or hydrophobized mica)¹. Due to high hydrophobicity of the PDMS surface the droplet of PE solution weakly interacts with the surface, while remaining “sticky” to the pipette. This fact allows to move the droplet in a desired direction with a controlled velocity simply by moving the pipette. Although visually the droplet does not wet the PDMS surface, an adsorption process obviously takes place leading to large-area patterns of oriented PE fibers. The size of the structures can be controlled by the deposition conditions. Thus-formed 1D structures can be easily transferred onto other surfaces by contact printing. Finally, these patterns can be used as templates for assembling of various species having affinity to the corresponding PE, such as amphiphiles. Also conductive polymers, like polypyrrole can be selectively polymerized along the molecules forming conductive nanowires.

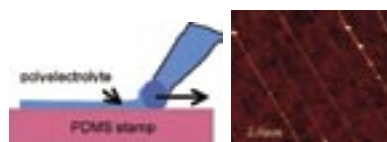


Figure 1. Schematics of the deposition process (left). TM AFM images of stretched and aligned structures of polystyrene sulfonic acid deposited at different concentrations (right).

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FUNSMART II — Low-dimensional Supramolecular Nanostructures by Design

Functional surfaces and nanostructures play an increasingly important role in nanoscience and nanotechnology. Here I report on the rational design of low-dimensional organic-inorganic hybrid nanostructures via supramolecular self-assembly of organic molecular building blocks at surfaces. We have fabricated 0-, 1- and 2-dimensional systems under ultra-high vacuum conditions by organic molecular beam epitaxy and used scanning tunnelling microscopy and synchrotron radiation X-ray spectroscopy to characterize these systems *in-situ*.

First we have investigated the assembly principles involving of different types of non-covalent interactions, e.g., hydrogen bond, ionic bond and metal-coordination. We demonstrate that the information stored in the individual molecular building blocks can be transferred to the supramolecular organization level in a controllable manner. Then we have applied these principles to fabricate nanostructures exhibiting pre-designed structures and properties. Last but not the least we have explored the potential functionalities of these low-dimensional supramolecular systems, e.g., nano-patterning, surface templating, low-dimensional magnetic systems, heterogenous catalysis, sensing or molecular recognition.

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SSATMN — Nucleation and growth of deposited metal nanoclusters

The nucleation, growth and coalescence of transition and noble metal clusters obtained by deposition of monoatomic beams onto an oxide surface under Ultra-High Vacuum (UHV) conditions are studied through a combined experimental and theoretical effort within the SSATMN/SONS project (<http://h2.ipcf.cnr.it/alex/ssatmn.html>).

From the theoretical side, a general protocol is developed which starts from first-principles calculations on small clusters both in the gas-phase and interacting with an oxide surface (including quantum mechanical algorithms to predict diffusion energy barriers and a density-functional global-optimization approach for determining cluster global-minimum structures), then derives computationally inexpensive, yet accurate metal-metal and metal-oxide potentials from an analysis of such calculations, and finally utilizes these potentials to study both static (global-optimization searches, etc.) and dynamic processes (nucleation, diffusion, growth, coalescence and melting, in the simplest cases via classical Molecular Dynamics, and rescaling the time scale in more complex instances via Accelerated Molecular Dynamics and kinetic Monte-Carlo approaches). From the experimental side, the nucleation, growth and coalescence of metal clusters is studied by a combination of different experimental techniques: Atomic Force Microscopy (AFM), Scanning Tunnel Microscopy (STM), High-Resolution Transmission Electron Microscopy (HRTEM), dynamic Scanning Force Microscopy (SFM), and Grazing Incidence Small Angle X-Ray Scattering (GISAXS). These techniques are used on the same systems to derive complementary information and to amplify in a synergic way the potentialities of the individual techniques. The outcome is a very thorough and detailed analysis, from which kinetic parameters (such as detrapping or diffusion energies) and morphological parameters (such as size, shape and inter-particle distance of the clusters) can be derived. The direct comparison between experimental and theoretical information on the actual cluster growth kinetics then cross-fertilizes each approach, and allows one to clarify its basic mechanisms. This combined experimental/theoretical protocol is exemplified with the growth of Pd clusters on the MgO(100) surface as a prototypical case study.

Additionally, emphasis is put on surface nanopatterning and magic clusters as tools for orienting the growth and obtaining narrow size and shape distributions, as supported by both experimental and theoretical evidence, focusing attention on the use of naturally nanostructured surfaces, such as Al₂O₃/Ni₃Al(111) or TiO_x/Pt(111), or of surfaces exhibiting a misfit dislocation network, such as MgO/Ag(100) and CoO/Ag(100).

Bimetallic clusters are finally considered, in view of the strategic character and promising applications of such systems (e.g., optical, mechanical and catalytic properties of core-shell nanoalloys). Selected properties of metal clusters are also investigated.

At variance with pure clusters, binary clusters can exhibit a richer behavior, and can also give rise to electronically and structurally “magic” structures.

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SPANAS — System for Photonic Adjustment of Nano-scale Aggregated Structures

The SPANAS consortia has worked with a number of different strands, which revolve around adaptive optics, micromanipulation and microfluidics. In this presentation an overview of our results will be given. More specifically, we have completed the following projects:

1. We have developed microoptical elements and systems for optical tweezing. Significant progress has been made in the integration of microoptical elements with microfluidics for optical manipulation. To this end diffractive optical elements have been designed, fabricated and replicated into a PDMS microfluidic channel system.
2. We have demonstrated the use of modal liquid crystal devices as 3D control elements of optical tweezers. We are now working on integrating these devices with planar integrated optics.
3. We have investigated particle motions in liquid crystal cells which are produced by laser induced local heating.
4. We have undertaken a number of experiments with particles trapped in counter-propagating beams. We have also produced an optical model to describe the results.
5. We succeeded in integrating The Generalized Phase Contrast (GPC) method for micromanipulation into a microfluidic system where trapping experiments are fully computer-automated and thereby capable of running with only limited supervision from a user. The system is able to dynamically detect living cells using a computer-interfaced CCD camera, and respond to this by instantly creating traps at positions of the spotted cells streaming at flow velocities that would be impossible for a human operator to handle.

Oral Presentation Abstracts

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MOL-VIC — One-dimensional supramolecular self-assembly on vicinal surfaces

Linearly shaped, conjugated molecules and vicinal surfaces can be combined to fabricate self-assembled supramolecular structures with one-dimensional anisotropy. Our collaborative research project has made a prospective work using a variety of molecule/surface combinations that have been tested using standard, powerful surface sensitive techniques, such as STM, photoemission and absorption, as well as theoretical calculations. Our most recent results open interesting avenues towards the control of the self-assembly process, i.e., the fundamental understanding of the hierarchy of molecule/surface interactions that governs the supramolecular self-assembly process.

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NOMSAN — Novel optical methods for self assembled nanostructures

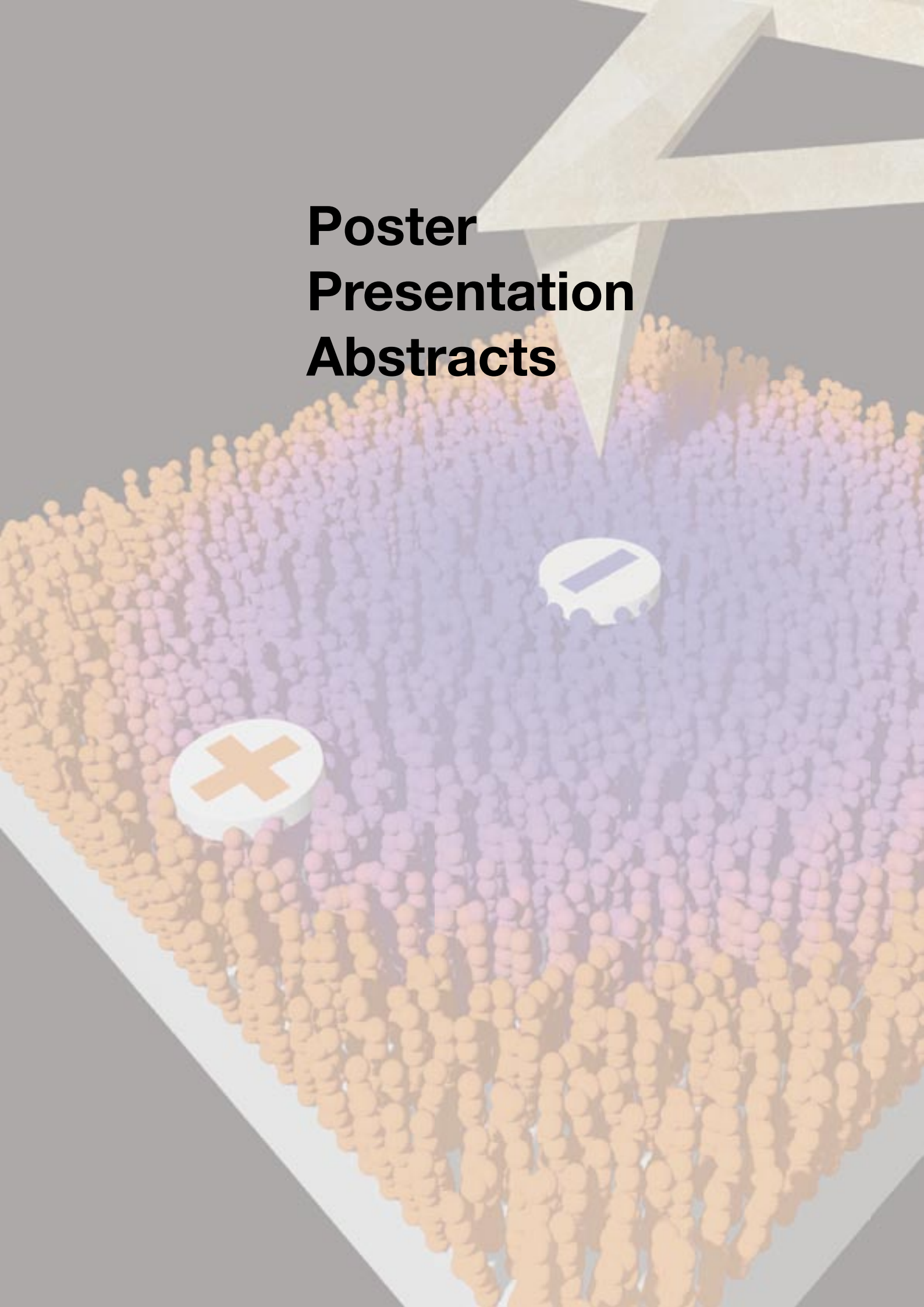
Optical tweezers is a powerful non-contact technique where micrometre sized particles can be grabbed, moved and generally manipulated solely with light. Optical tweezers have forged an important bridge between physics, chemistry and biology. In recent years there has been a proliferation of activity in this area, fuelled, in part, by the recognition that we need to advance the “optical toolkit”. This essentially means creating an optical landscape and enhancing our ability to move and sort particles and importantly, create 2D and 3D arrays of particles.

This talk will give an overview of the advances made by this consortium under the NOMSAN project. This will include work on optical binding of particles, the creation of large scale arrays using evanescent waves and sorting of objects and studies of metallic nanoparticles and exploiting surface plasmon resonances.

Selected references from the NOMSAN project. (Please see websites www.icfo.es and www.st-and.ac.uk/~atomtrap for more details and further references)

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Poster Presentation Abstracts



Poster Presentation Abstracts

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AMPHI — Structures of Block Copolymer Thin Layers

Block copolymer systems are – thanks to some of their advantages – at present time in great focus of science and industry because of their great potential to be used in various applications. On one side, the ability of block copolymers to form organized nanoscaled structures induced by microseparation is a fundamental requirement to be used in nanotechnology. On the other side, there exist relatively easy ways to tune physical and/or chemical properties of a system directly at the polymerization or by additional functionalization. By this way it is possible to prepare structured materials with suitable properties usable in biomedical- or nano-applications.

In our experiment we stay focused on surface patterns formation in the block copolymer thin layers. We have used vapor-treatment in common organic solvents and studied newly created formations. We have paid attention to system long-range organization, which is one of the requirements to produce nanostructures like nanodots, nanowires or even inert skeleton usable e.g. as a carrier in cells cultivation for wound dressing or bone or organs replacement.

The polymers used were styrene and methacrylate derivatives, namely poly(4-octylstyrene)-b-poly(n-butylmethacrylate), poly(4-octylstyrene)-b-polymethylmethacrylate and poly(styrene)-b-poly(styrene-co-acrylonitrile). The layers were prepared by dip-coating from toluene solutions. We have used the Tapping-Mode AFM method to observe changes at originally smooth surfaces after modification, and small-angle X-ray scattering to assess the bulk structure.

We have confirmed that the method of vapor treatment of thin layers can be used with suitable block copolymer materials to induce various surface shape formations.

We acknowledge support by the Grant Agency of the Czech Republic within the EUROCORES Programme SONS of the European Science Foundation, which is also supported by the European Commission, Sixth Framework Programme.

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BIONICS — DNA Block Copolymers: From Synthesis to Interactions with Living Cells

A synthetic strategy for the generation of amphiphilic linear, single stranded (ss) DNA block copolymers will be presented. The morphologies which are adopted by these materials will be discussed. Special attention will be paid to engineering the structural properties of micelles by hybridization. [1]

In the context of applications regarding DNA block copolymers, programmable, sequence specific organic reactions in spherical micelles will be presented. [2] Furthermore, the interactions of these micelle systems with cells were studied regarding uptake behaviour and their use as drug carriers.

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Poster Presentation Abstracts

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BIONICS — DNA Self-assembled Supramolecular Structures on long single-stranded Carrier Strands

The intrinsic self-assembly capability of DNA is a versatile and powerful tool towards the construction of nanoscale objects. The strictly information-driven pairing of DNA fragments can be used to rationally design and build nanostructures with planned topologies and geometries. Taking advantage of the steadily expanding library of well-characterized DNA motifs, numerous examples of structures with a variety of shapes have appeared in the literature in the last few years, laying the foundations for a very promising DNA-mediated bottom-up approach to nanotechnology.[1] Stepwise "hierarchic" assemblies can also be implemented to obtain DNA structures with an high degree of complexity. [2]

Several different applications for DNA self-assembled structures have been proposed and prototyped in the past few years. [2-4] Rationally designed two-dimensional DNA scaffolds have been employed for the sequence-dependent immobilization of proteins and metal nanoparticles; one-dimensional scaffolds have been also used for immobilization, or metallized to produce nanoscale conductive wires.

For many applications it would be advantageous to produce arbitrarily long, one-dimensional, mechanically rigid DNA scaffolds with designed sequences. In this context, double helical DNA is often too flexible to be used as a reliable scaffold, and is not readily available for hybridization to a target sequence. The design and synthesis of rigid DNA 'tiles' based on various motifs, and their successive polymerization into rigid chains allows to circumvent this limitation. [2] However, the length of the resulting supramolecular polymer is heavily dependent on the type of interaction between individual tiles. One way to avoid this limitation is to assemble tiles on a long "carrier" single-stranded DNA molecule. Rolling Circle Amplification (RCA) is a powerful method to produce these ssDNA carrier strands. [5]

In this communication, we first describe the design and synthesis of a class of DNA supramolecular constructs resulting from the polymerization of a self-complementary tile in different controlled conditions. [6] This module is a DNA parallelogram constituted by six oligonucleotides that upon thermal annealing self-assemble into the desired shape. Each parallelogram can bind to exactly two other parallelograms by means of a pair of cohesive sticky ends, resulting in a one-dimensional array of DNA modules. The sticky ends linking successive tiles are designed so that, the same tile monomer can afford supramolecular polymers with different shapes when annealed in different conditions. [6] Then, we discuss how the same tiles can assemble on a long ssDNA carrier produced by RCA and how this affects the resulting structures. We also discuss the use of long ssDNA carriers for the assembly of other types of DNA self-assembled nanostructures.

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BIONICS — Electrical Characterisation of Helical Chromophoric Nanowires

The electronic transport properties of a perylene-substituted polyisocyanide material are examined, using thin-film transistors. The devices are found to exhibit reproducible n-type transistor behaviour, with bulk mobilities and on/off ratios of the order of 10^{-4} cm²/Vs and 10^5 respectively. The electron injection properties of the Au electrodes are found to be significantly improved by a thiol self-assembled monolayer (SAM) treatment, in accordance with our cyclic voltammetry studies of the semiconducting material. We report experimental differentiation and modelling of the intra- and inter-chain transport processes, with the goal of understanding intra-chain transconductance, in the context of potential next generation materials for single-strand molecular electronics.

Poster Presentation Abstracts

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Fun-SMARTs I — Lithographically controlled self-organization of supra-molecules and functional materials in thin solid films

Here we present how bottom-up nanofabrication techniques can induce self-organization improving some physical properties of thin solid films via nanostructuring. We focus our attention on the nanopatterning and integration in electronic devices for a variety of technologically relevant materials and supramolecules, in particular we have studied: conjugated oligomers and polymers, molecular magnets, spin crossover compounds, and rotaxanes.

Our processes take advantages from spontaneous self-organizing properties of materials and supramolecules; they allow us to pattern soluble materials with nanometer-sized structures in single step and in a few seconds. We demonstrate patterning nanostructures like droplets [1,2], stripes [3], nanorings [4] and fibers, with size features at the nanometric range.

In order to fabricate nanostructures Our processes exploit, crystallization of organic semiconductors [3], demixing [5] and dewetting [4] of molecular magnets, spatial controlled dewetting of rotaxanes [1].

In the second part of the seminari we demonstrate a direct application of our techniques on field effect transistor, ordered nanopatterning and for information storage.

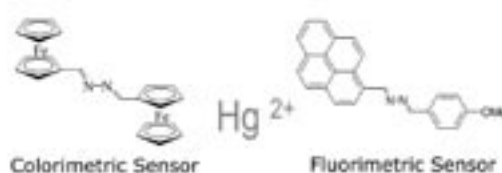
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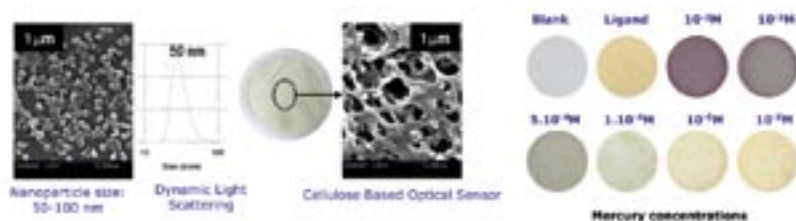
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FunSMARTs I — Organized Nanostructures for the Fabrication of Cellulose Based Mercury Sensors



Mercury is a unique element due to its tendency to form toxic compounds at trace levels in the environment. Mercury levels are continually being monitored by government agencies resulting in increasing stringent requirements for lower trace level mercury determinations. With this aim, we have synthesized a family of molecules with metal ionic sensing capabilities [1]. Our target molecules consist of disubstituted diaza butadienes which depending on the substituents yield combined optical, fluorescent and redox sensor capabilities in a sensing molecule. With these compounds it has been possible to check for the first time the ability of the azine bridge to complex Hg^{2+} selectively in aqueous environment which is very important for environmental issues.

In the literature, there are not many selective molecular mercury sensors, and the number of these, able to detect low levels of mercury supported on a solid substrate is limited. With this aim nanostructures of the substituted diaza butadiene sensing molecules have been obtained and used to be firmly attached and uniform coated on a membrane filter in order to obtain hybrid cellulose membranes that work as highly sensitive and selective mercury sensor devices [2]. Very thin and pure sensor membranes provide a highly concentrate signalling surface, which leads to high sensitivity of this system. Moreover, water-permeable sensor-coated membranes allowed naked-eye detection down to ppb concentrations of mercury ions by combining filtration enrichment of samples with colour signalling. The result is accurate, sensitive and cost-effective mercury determinations.



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Poster Presentation Abstracts

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FunSMART I — Supramolecular Fe(II) High Temperature Spin Transition (ST) Architectures

Amongst the group of magnetic phenomena, the spin transition (ST) of six coordinated Fe(II) compounds witnesses broad attention due to its diverse change in physical properties (magnetism, colour, structure, etc.), which can be triggered by applying external field parameters to the macroscopic samples [1]. The use of supramolecular synthetic techniques (H-bonding, coordination polymers, reversible coordination etc.) might expand the range of available molecular ST objects giving access to novel molecular properties [1,2].

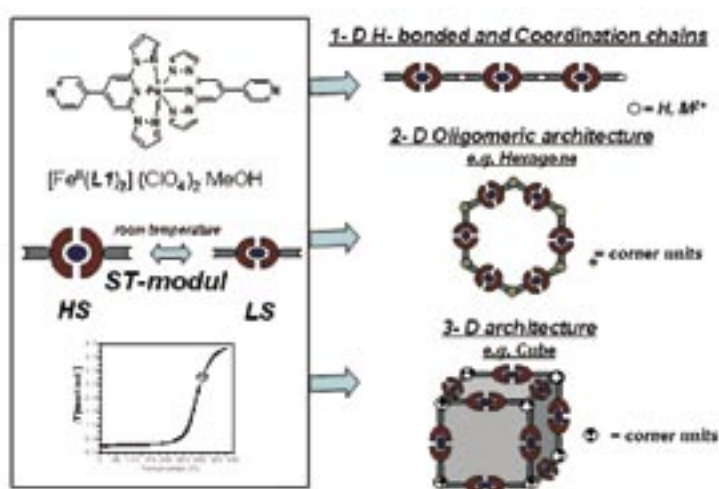


Figure 1. Synthesis of ST module and some of the possible higher dimensional architectures.

Here we present the synthesis of 4-substituted-2,6-dipyrazolylpyridine Fe(II) based ST module, which were used in supramolecular reactions to build-up switchable 1D, 2D and 3D architectures (Figure 1). For example, we used $[\text{Fe}^{\text{II}}(\mathbf{L1})_2\text{H}](\text{ClO}_4)_3 \cdot \text{MeOH}$ ($\mathbf{L1}$ = (4'-4''-pyridyl)-1,2':6'1''-bispyrazolylpyridine), to form 1-D hydrogen bonded $[\mathbf{N} \cdots \mathbf{H} - \mathbf{N}]$ chain, which exhibit ST around room temperature. The dependence of the ST properties on the structure of the obtained supramolecular entities will be discussed in detail using X-ray crystallography, magnetic measurements, and Mössbauer investigations.

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Keywords: Self assembly,
hydrogen bonded
supramolecular scaffolds

FunSMARTs I — Supramolecular Functional Materials from Hydrogen-Bonded Scaffolds

The design and construction of a variety of functional nanomaterials from supramolecular hydrogen bonded scaffolds is very interesting [1]. Their immobilization and controlled multi-dimensional arrangements on solid supports as well as their application as scaffolds in solution are under intense investigation. Our focus is on the molecular level investigation, organization and the surface morphology of these nanostructures. We have reported the self-organization of the multi-component hydrogen-bonded rosette assemblies into ordered nanostructures on highly oriented pyrolytic graphite (HOPG) surface [2]. Further, these nano-constructions are utilized as self-assembled scaffolds for attaching 'functional groups' or constructing metal containing nanostructures of higher hierarchical order [3], for example, silver or gold containing rosette nanostructures [4]. Employing such templates as an alternative to usually applied supramolecular templates, for instance DNA strands and peptide nanotubes [5], to direct the formation of metallic nanostructures on surfaces may lead in the future to versatile paths for fabricating electrically conducting nanowires. Moreover, we apply these supramolecular structures as mediators for assembling the metal nanoparticles in solution in 3-D [6]. The morphology and the optical properties of these multidimensional nanostructures are tunable. Thus we present the feasibility of these hydrogen bonded scaffolds for creating a variety of functional materials. Positioning and patterning of such functional nanostructures by self-assembly processes could open the path in realizing the molecular devices.

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Poster Presentation Abstracts

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MOL-VIC — Adsorption of pentacene on Cu(110): self-assembling and electronic structure

The relative importance of molecule-molecule vs. molecule substrate interaction manifests itself in the formation of ordered structures of molecules on metal surfaces. Planar aromatic hydrocarbon molecules like tetracene, pentacene or anthracene lack the ability to form hydrogen bonds. The resulting networks depend on the shape of the molecule and the detailed atomic structure of the end groups, although particular configurations can be forced by the morphology or the electronic structure of the substrate. Due to this fact, when adsorbed on metal surfaces, planar aromatic hydrocarbon molecules become an interesting model system to investigate the relative importance of each interaction. In this work we report an investigation on the adsorption of pentacene on Cu(110) using angle-resolved photoemission with synchrotron radiation, scanning tunnelling microscopy, and low-energy electron diffraction. We study the self assembly of pentacene molecules in the low to intermediate coverage range. Different long range ordered surface structures are observed as a function of surface coverage [1]. On the basis of these data, we analyze the role of the surface electronic structure in the process of self-assembling as a function of coverage and for the different surface structures observed [2].

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MOL-VIC — Identifying isomerization - combined experimental and theoretical NEXAFS studies

When studying the isomerization of molecules, identification and distinction of the different isomers is a critical issue. Here cis- and trans-Stilbene are a model system for "molecular switches". We have investigated their adsorption on semiconductor and metal surfaces, and for comparison, in gas-phase. In this work we demonstrate the use of NEXAFS-spectroscopy as a versatile tool to investigate the interaction of the molecules with the surface and the arising consequences for isomerization. NEXAFS-spectra of the molecules in gas-phase show spectral features in the π^* -resonance that allow for a clear distinction of the isomers. Upon adsorption on surfaces these spectral features remain unchanged - thus clearly identifying the isomers - while the σ^* -resonances and the higher π^* -resonances undergo changes. In combination with theoretical calculations these changes can be used to identify the interaction of the molecules with the substrates and to reveal the adsorption geometry. Furthermore the implication of adsorption on the photoinduced isomerization, especially the inhibition of the isomerization-pathways known for gas-phase and solution, is explained.

Poster Presentation Abstracts

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MOL-VIC — Controlled contact to a C₆₀ molecule

The tip of a low-temperature scanning tunneling microscope is approached towards a C₆₀ molecule adsorbed at a pentagon-hexagon bond on Cu(100) to form a tip-molecule contact. The conductance rapidly increases to ~ 0.25 conductance quanta in the transition region from tunneling to contact. *Ab-initio* calculations within density functional theory and non-equilibrium Green's function techniques explain the experimental data in terms of the conductance of an essentially undeformed C₆₀. The conductance in the transition region is affected by structural fluctuations which modulate the tip-molecule distance.

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NANOSMAP — Selective Surface Modification via Oligo(ethylene oxide) Derivatives

The control of interfacial interactions between a synthetic material or device and a biological medium is an important aspect of the design of biomaterial and biosensor surfaces. Resistance to non-specific protein interactions (“protein-resistant” or “non-fouling” surfaces) is a particularly relevant issue in applications ranging from devices such as blood contacting cardiovascular stents to biochips in medical diagnostics to model surfaces such as cell-adhesive patterns in an inert background for fundamental cell-surface studies. Poly(ethylene glycol) (PEG) has been extensively used for this purpose in view of its low toxicity and low immunogenicity. PEG immobilized on a surface has the ability to prevent non-specific bio adhesion, such as protein adsorption, bacterial adhesion and cell attachment.[1]

Novel oligo(ethylene glycol) based derivatives, containing either a phosphoric acid or phosphonic acid group as well as an long alkyl chain were synthesized with the aim to produce self-assembled monolayers (SAMs) on metal oxide surfaces to prevent non-specific adsorption of bio molecules. The use of alkyl phosphorous acid derivatives opens a practical route to build molecular thin films on inorganic metal oxide surfaces, like TiO_2 and Al_2O_3 . When the substrate surface consists of mixed $\text{TiO}_2/\text{SiO}_2$ structures the molecules should only adsorbed onto the metal oxide areas. Therefore, we are able to get a structured substrate, where TiO_2 is covered by an monolayer, whereas SiO_2 remains free.

We varied kind of terminal, functional group, oligo(ethylene glycol) unit, and alkyl chain length to study the differences in adsorption behaviour and layer formation using contact angle measurements, surface plasmon resonance spectroscopy (SPR), angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and spectroscopic ellipsometry (VASE).[2] The stability of the adsorbed layers is tested in different buffer systems. Finally, the protein resistance of the treated substrates is investigated by application of suitable protein molecules.

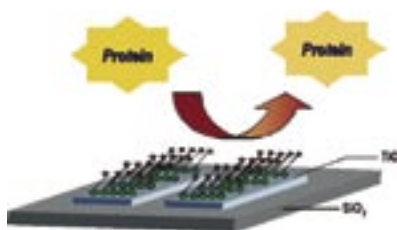


Figure: Illustration of selective adsorbed SAM's on TiO_2 surfaces and protein resistance

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Poster Presentation Abstracts

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NanoSMAP — Creating Protein Nanopatterns Using Controlled Particle Self-Assembly

Nanopatterns are becoming increasingly popular in the field of bioscience and bioengineering because they provide novel tools to address biological problems. For example, protein nanoarrays not only enable molecular level statistics of binding events but also offer an increased sensitivity compared to microarrays.[1] Many techniques have been developed for the creation of nanopatterns.[2] However, sample preparation with most techniques remains prohibitively expensive for large area applications due to need for complex equipment and serial processes. With this work we aimed at developing simple and inexpensive, but still versatile, nanopatterning techniques with possible applications in the field of nanobiotechnology. Various particle self-assembly techniques were investigated for the creation of nanopatterns. Micron and sub-micron sized polystyrene (PS) particles were for example assembled by dip-drying from aqueous suspensions or guided to self-assemble in microfluidic channels.

The former technique allows us to achieve monolayer coverage in large hexagonal lattices on flat surfaces. Such particle patterns were then tailored by reactive ion etching to linearly reduce the size of the particles. It was possible to produce ordered PS features of different sizes and separations by varying the etching time and initial particle diameter. The tailored particle patterns created via dip-drying and etching were later transferred into the substrate by etching creating nanopillars. These could be produced also with a chemical contrast, leading to e.g. titania pillars in a silica background. With a selective molecular patterning method[3] we further transferred the chemical contrast into a biochemical contrast creating protein and other self-assembled nanopatterns.

When assembling the particles in microfluidic devices it was possible to transfer the particle pattern to the substrate creating protein patterns with no underlying chemical or topographical pattern via a new technique called wet particle lithography. All steps of this patterning technique were performed in aqueous solution and are therefore gentle to the involved proteins. Already with simple designs of microfluidic devices sample chips may be patterned with many different proteins at once. Keywords: self-assembly, particles, nanopatterning, nanoarray, biofunctionalization.

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NEDSPE — Nanoscale electronic devices via templating supramolecular polyelectrolytes

We present novel method to fabricate one-dimensional (1D) self-assembled monolayers and multilayers (SAMs) of (12-pyrrol-1-yl-dodecyl)-phosphonic acid (Py-DPA) on various polar surfaces using polyelectrolyte nanostructures as positive templates. Particularly, we demonstrate that i) patterns of aligned 1D polycation structures on a poly(dimethylsiloxane) (PDMS) stamp can be prepared simply by moving the droplet of the polycation solution along the surface; ii) these patterns can be used as templates for assembling of Py-DPA having in water the charge opposite to the charge of the template; iii) Py-DPA SAMs can be then transferred onto mica or silica-wafers by printing. We believe that these nanostructures having polymerizable pyrrole head-group might be useful for creation of electrically conductive patterns of conjugated polymers.

Poster Presentation Abstracts

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NETSOMA — Multi-component semiconducting polymer systems with low crystallization-induced percolation threshold

In various applications of polymers, blends and other multi-component systems are employed in order to meet multiple requirements which cannot be fulfilled by a single material. For instance, in polymer optoelectronic devices it is often highly desirable to combine the semiconducting properties of the conjugated species with the excellent mechanical properties of certain commodity polymers. To this end, so far, most efforts on bi-component systems have concentrated on use of amorphous-amorphous and amorphous-crystalline materials combinations, whereas exploration of crystalline-crystalline binaries have been relatively rare. This is rather surprising as the crystalline nature of the components may provide a significantly broader range of means to control the microstructure and, hence, properties of the final object when compared to systems comprising amorphous species. Here we investigate bi-component blends and diblock copolymers comprising semicrystalline regio-regular poly(3-hexyl thiophene) (P3HT) and selected semicrystalline commodity polymers, and show that due to a highly favorable, crystallization-induced phase segregation of the two components, during which here the semiconductor is predominantly expelled to the surfaces of cast films, vertically stratified structures can be obtained in a one-step process. Incorporating the latter as active layers in polymer field-effect transistors (FETs), we find that the concentration of the semiconductor can be reduced to values as low as 3 wt% without any degradation in device performance. This is in stark contrast to conjugated polymer systems comprising an amorphous insulating polymer, for which significant reduction in electrical performance was reported. Crystalline-crystalline/semiconducting-insulating multi-component systems offer an expanded flexibility for realizing high-performance semiconducting architectures at drastically reduced materials cost and with, among other things, enhanced mechanical properties and improved environmental stability without the need to design all performance requirements into the active semiconducting polymer itself.

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NOMSAN — Parallel and selective trapping in a patterned plasmonic landscape

Conventional optical manipulation uses the gradient optical forces to trap an object in the focus of a 3D laser beam. Within a perspective of miniaturization, the implementation of optical tweezers at a surface opens a huge potential towards the elaboration of future lab-on-a-chip devices entirely operated with light. The transition from 3D to 2D is rendered possible by exploiting evanescent fields bound at interfaces. Particularly, Surface Plasmons (SP) at metal/dielectric interfaces are expected to be excellent candidates to relax the requirements on incident power and to scale down trapping volumes down to the nanoscale.

Here we report on novel 2D SP-based optical tweezers formed by finite gold areas fabricated at a glass surface. We demonstrate that SP fields enable stable trapping of single dielectric beads under a non-focused illumination with considerably reduced laser intensity compared to conventional optical tweezers. Our analysis including simulations based on the Green Dyadic method suggests trapping is governed by enhanced SP optical forces assisted by local thermal convection arising from the heat dissipation in the metal. We show the method can be extended to parallel trapping over any predefined pattern. Finally, we demonstrate how SP-tweezers can be designed to selectively trap one type of particles out of a mix, acting as an efficient optical sieve [1].

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Poster Presentation Abstracts

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NOMSAN — Transverse Optical Binding of Self-Organized Colloidal Arrays

Large-scale optically-induced ordering in colloidal systems, mediated by optical binding, is a fascinating effect which has been observed experimentally, but whose underlying physics is very poorly understood[1, 2]. Optical binding occurs when a colloidal particle, trapped in an optical potential, perturbs the incident field to create stable trapping points for adjacent particles to occupy[3]. For large numbers of particles this leads to extended periodic arrays of mutually interacting particles, which may support a host of different coherent interactions and non-linear effects. The difficulty in understanding the physics of the inter-particle interactions in optical bound matter is the complexity of the system, which makes it impractical to solve using traditional modelling techniques. In this paper we experimentally and theoretically investigate the self-organization of optically bound colloidal arrays in the presence of counter-propagating cavity enhanced evanescent waves[4]. We develop a nonlinear optics based theory which suggests that the colloidal arrays formed along the laser propagation axis are linked to the break-up of the incident field into arrays of spatial optical solitons, and that the transverse spacing of the optically bound arrays is related to the spatial period of a transverse modulation instability of the nonlinear coupled light-matter system. These results represent an explicit and novel demonstration of the recently suggested phenomena of spatial optical solitons in soft condensed matter[5]. It is our firm belief that the experimental system that we have developed here is an excellent platform for exploring more general properties of optically-induced nonlinear instability in colloidal systems; provide further insight into the origin of large-area organization of optically bound matter; and better understand the link between these two previously disparate effects.

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SALDSON — Step-Ordering in Semiconductor Quantum Nanostructures Grown on Patterned Substrates

High-quality III-V semiconductor quantum wells (QWs) with narrow photoluminescence (PL) linewidths and high electron mobilities are central to fundamental studies and a number of device applications. The optical and electrical transport properties of such QWs and other semiconductor nanostructures are determined by the extent of impurity incorporation and the quality of their interfaces. Although III-V QWs are typically produced by molecular-beam epitaxy, growth by metallorganic vapor-phase epitaxy (MOVPE) provides an attractive alternative in view of its advantages in a production setting and the possibility for making novel quantum wire and quantum dot structures.

In this poster we will describe recent experiments and an accompanying theory for the growth of GaAs/AlGaAs QWs produced by MOVPE on slightly misoriented substrates. The small misorientation is sufficient to modify the growth mode and surface morphology of the epilayers, which has a significant effect on the optical and transport properties. Measurements have revealed low-temperature PL linewidths as low as 0.6-meV and low-temperature electron mobilities greater than $10^6 \text{cm}^2/\text{Vs}$ in GaAs/AlGaAs QWs produced by MOVPE on slightly misoriented substrates [1].

We have developed a model that accounts for the surface morphologies seen by in these experiments, ranging from nucleation and growth of islands on terraces to different types of step bunching. Our model is based on the following schematic MOVPE sequence. TMGa and AsH₃ arrive at the substrate by diffusion through a boundary layer, after which these species and any of their fragments migrate with minimal lateral interactions to step edges, where they release Ga and As through decomposition reactions. The highly mobile surface species can lead to step-flow growth with terrace lengths of up to several microns, which prevents the direct simulation of this scenario, but presents no problem to a formulation in terms of our (one-dimensional) Burton-Cabrera-Franck (BCF) type equations. The model includes only the most basic kinetic steps, but is nevertheless able to reproduce quantitatively the trends in the morphology observed in experiments.

The observation of step ordering on patterned, slightly misoriented substrates and its interpretation using kinetic Monte Carlo simulations will [2] also be discussed.

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SASMEC — Measuring the conductance of molecular junctions

As a clean gold contact breaks its conductance decreases stepwise. The conductance of the last step is typically $G_0=2e^2/h$, the so-called quantum of conductance, indicating that the contact consists of only one atom or single atomic chain. After rupture the conductance decreases exponentially which is the signature of tunneling. As a consequence, a conductance histogram shows a prominent peak at G_0 [1].

In contrast, when a gold contact is broken within a molecular solution, additional conductance steps at values lower than G_0 appear. The corresponding peaks in the conductance histograms have been associated with the conductance of a single molecule bridging the gap between the electrodes.

We have measured the conductance of several molecules amine terminated alkane chains in solution at room temperature using a scanning tunnelling microscope (STM). Our setup has been modified to allow for the measurement of the conductance continuously spanning 6 decades in contrast to the conventional 4 decades. This facilitates the control of the pulling process and the range of conductance that it is possible to measure. In addition we have developed a convenient analysis method in terms of the average tunneling exponent as an alternative to the conventional conductance histograms.

Our results are in good agreement with recent results [3,4]

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SASMEC — Self-organization of bacterial cytoskeleton proteins on surfaces

Cytoskeleton proteins are nanometer sized soluble proteins that play an essential role in maintaining cell shape. The polymerizing units are protein monomers or dimers, usually a few nanometers in diameter, that, in the presence of a phosphorylated nucleotide (ATP or GTP) are capable of self-organizing into larger structures that can incorporate up to a few hundred monomers. The polymers formed are usually dynamic structures that undergo continuous exchange of material with the soluble proteins available in the medium. The detailed interaction between the self-aggregating monomers or dimers, controlled partly by the phosphorylated state of the nucleotide, determines the rate and form of exchange. Actin and tubulin, two eukaryotic cytoskeletal proteins, have been extensively studied and characterized [1].

Bacterial cytoskeleton proteins have been described more recently and their self-aggregating properties have not yet been fully characterized. One of the bacterial cytoskeleton proteins, FtsZ, plays an essential role in cell division [2]. It is a soluble 40 kD protein with GTPase activity that is structurally analogous to eukaryotic tubulin. This protein localizes on the inner side of the cytoplasmic membrane during bacterial cell division at the midcell point and forms a dynamic ring that is essential for the recruitment of other proteins the multiprotein complex called the septosome responsible of dividing the cell through the middle to form two new daughter cells.

We have used atomic force microscopy to characterize the shape and dynamic behaviour of individual *E. coli* FtsZ protein filaments formed on a mica surface. We describe and model their shape and dynamic restructuring as the nucleotide is being consumed [3]. Filaments showed a strong tendency to curve and to interact laterally. Given that FtsZ interacts with the inner cytoplasmic membrane of the bacteria through its interaction with the membrane protein ZipA, we have also explored its behaviour on a mica surface covered with a lipid bilayer with the ZipA protein incorporated in the bilayer with a controlled orientation. FtsZ shows no affinity for lipid bilayers of different composition, but is able to attach and polymerize on a lipid surface in the presence of oriented ZipA.

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SONS-AMPHI — Janus Discs

Janus structures are colloidal particles which possess two phase-segregated compartments of different chemistry or polarity.[1-3] Recently, we have been able to synthesize disc-like Janus particles via a template-assisted process based on microphase-separated polystyrene-block-polybutadiene-block-poly(tert-butyl methacrylate) terpolymer structures (see Figure 1). After crosslinking of the polybutadiene middle block, the size of the disc-like Janus structures can be tuned simply by sonication. Upon acidic hydrolysis of the protective tert-butyl groups, truly amphiphilic Janus discs, carrying polystyrene and poly(methacrylic acid) chains, can be obtained. These structures can be transferred into aqueous media via a simple dialysis procedure.



Figure 1: Schematic synthesis of Janus discs, based on the selective crosslinking of PB domains of a SBT terpolymer with lamella-lamella (ll) morphology.

Due to the non-centrosymmetric arrangement of the corona, both the non-hydrolyzed as well as the hydrolyzed particles can undergo self-assembly processes into superstructures. Different kinds of superstructures are formed depending on the size of the disc-like Janus particles. These novel self-assembled structures have been investigated with scanning force microscopy, scanning electron microscopy, cryogenic transmission electron microscopy and dynamic light scattering. Additionally, the particles show a strong influence on the oil/water interfacial tension and are thus suitable as future surfactants. To further explore this effect, the hydrolyzed Janus discs were employed as surfactants for emulsion polymerization.

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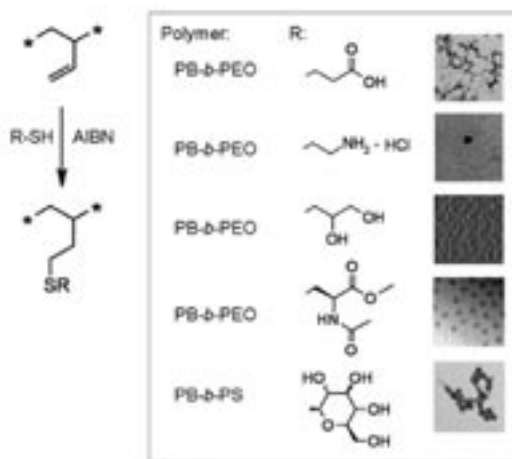
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SONS-AMPHI — Aggregation of hydrophilically modified polybutadienes

A toolbox of hydrophilically modified polybutadiene homopolymers and block copolymers was prepared by free-radical addition of α -functional mercaptans; functional groups included carboxylic acid, amine, ethylene glycol, amino acid, and glucose. Polymers could be directly dispersed in water under the formation of micelles or vesicles, as demonstrated by scattering experiments and microscopy.



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Poster Presentation Abstracts

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SPANAS — Integrated complex optical microsystems for biotechnology

The work of the collaborative research project (CRP) called „System for Photonic Adjustment of Nano-scale Aggregated Structures (SPANAS)“ is focused on the technical development of tools for micromanipulation and microfluidic systems specifically on generalized optical tweezers. The work is important for the study of nano-scale colloidal structures for practical applications such as photonic crystals, large array systems, switches, micro-fluidic processes and bio-chemical sensing devices.

Within the SPANAS CRP the Technische Universität Ilmenau coordinates work on integrated hybrid optofluidic microsystems. The results of the close cooperation with our partners at the University of Göteborg are presented[1]. We demonstrated the fabrication and functionality of lithographically fabricated diffractive optical elements integrated into the fluidic channels of a microfluidic system. Thus, it was possible to optimize the interface between the microfluidic channel system and the optical systems used e.g. for micromanipulation or optical sensing. We present the results of multiple optical tweezing experiments in such integrated microoptofluidic systems and discuss the further potential of the approach[2,3].

For the implementation of adaptive functionality in planar integrated microoptical systems we employed adaptive modal liquid crystal (LC) lenses[4]. In cooperation with the project partners of the University of Durham we developed and fabricated modal LC microlenses and microprisms. Those adaptive LC microelements were successfully combined with integrated planar optical microsystems. Good optical properties could be achieved over a reasonably large tuning range of several mm. We present the optical systems design as well as the experimental results for the achieved point spread functions[5,6].

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SPANAS — Micromanipulation at Durham

We describe work at Durham, UK, performed as part of the SPANAS project. This work involves a variety of projects all centered around the use of adaptive optics in micromanipulation experiments.

We present work on optical tweezing using liquid crystal modal elements, wavefront sensing of optical vortex beams, and anomalous particle motions within heated liquid crystal cells.

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SSA-TMN — Metal clusters on the regular and defected MgO(100) surface: a theoretical study of their structure and growth

The lowest energy structures of small pure (Ag, Au and Pd) and binary (Pd-Ag and Pt-Ag) metal clusters grown on the MgO(100) regular and exhibiting neutral point defects (Fs-centers and double vacancies) surface are determined through a Density-Functional global optimization (DF-GO) scheme based on a basin hopping search algorithm[1]. The results of such calculations are used to perform a detailed analysis of the mechanism of the growth and diffusion of the metal clusters on the oxide support.

Small clusters are characterized by a high mobility on the regular surface[2,3]. The diffusion energy barriers are calculated at the DF level by applying the NEB (Nudged Elastic Band) approach: the resulting barriers are in fair agreement with those extrapolated by an analysis of the cluster density observed in recent MBE experiments[4].

For Pd, already the interaction with the regular surface is sufficient to stabilize pseudomorphic arrangements at very small sizes ($N \geq 10-15$) with the concurrent formation of “structural defects” (truncation of vertexes, basal corners), whereas overhangs start forming at slightly larger sizes ($N \geq 23-30$) [5]. Surface defects (such as neutral oxygen vacancies, Fs-centers, and MgO divacancies) play an important role as trapping centers for metal atoms and small clusters[6,7]. As an example, a topographic analysis of the neutral Fs-defect reveals a large basin of attraction extending its influence up to 2nd and 3rd neighbors and with approximately cylindrical symmetry[8], resulting in a growth characterized by “rotational invariance” and “double frustration”. The corresponding high fluxionality corresponds to the existence of several different structural motifs in a small interval of total energy.

At variance with pure clusters, binary clusters can exhibit a richer behavior, and even give rise to electronically and structurally “magic” structures.

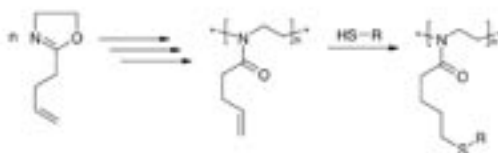
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BIOSONS — ‘Click’ modification of poly[2-(3-butenyl)-2-oxazoline] with mercaptans: A modular approach toward well-defined functional polymers

The modular synthesis of functional polymers[1] through ‘click’ modification of poly[2-(3-butenyl)-2-oxazoline] is described (see Scheme 1). Poly[2-(3-butenyl)-2-oxazoline] with very narrow molecular weight distribution (PDI < 1.1) was prepared by living/controlled cationic polymerization. Pendent double bonds were modified by free-radical addition of ω -functional mercaptans; functionalities included ester, carboxylic acid, and amino acid. This reaction proceeded in the absence of any side reaction, producing highly functionalized and chemically uniform polymers (justifying the term ‘click’, as introduced by Sharpless et al.[2]).



Scheme 1. Synthesis and ‘click’ modification of poly[2-(3-butenyl)-2-oxazoline]. As was demonstrated recently, poly(2-oxazoline)s can be interesting materials for studying the bioinspired formation of hierarchically ordered structures.[3]

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Poster Presentation Abstracts

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BIOSONS — Nucleo-copolymers Nucleotide-Based Amphiphilic Diblock Copolymers

How is Nature creating functional devices? For example, it is intriguing to realize that only four nucleic acids are needed to code the genetics of human beings. There, functionality is highly inherent to the nucleotide sequence. One single defect in this code may lead to serious diseases.

Currently, synthetic polymers represent a highly versatile class of materials due to the relative ease of controlling their composition, structure and properties. However, despite promising bio-mimetic approaches, the synthesis of complex polymers is far from reaching the high level of precision achieved by Nature on the synthesis of bio-macromolecules, which prevents their subsequent hierarchical organization into highly functional structures.

To overcome this issue we recently implemented the use of entities produced by Nature itself to drive the self-assembly of macromolecules into functional structures in the nanometer size range.

For the first time, the conjugation of a hydrophobic polymer segment to a sequence of nucleotides has been performed. Poly(butadiene) was covalently linked to a nucleotide sequence and the resulting nucleo-copolymer exhibits amphiphilic properties. In dilute aqueous solution, nanometer-sized spherical structures are detected by microscopy, which indicates that this nucleotide-based amphiphilic diblock copolymer self-assembles into spherically closed nucleo-copolymer shells, i. e. vesicular structures.

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BIOSONS — Biofunctionalization by spontaneous adsorption of proteins



In recent papers we showed that large amounts of proteins can be embedded into spherical polyelectrolyte brushes (SPB) by direct adsorption of the protein from solution.[1-3] The spherical polyelectrolyte brushes consist of a solid polystyrene sphere onto which long polyelectrolyte chains are densely grafted. The adsorption of BSA and other proteins was studied at various pH and at different concentrations of added salt.[1] Surprisingly, we observe strong adsorption of BSA onto the SPB despite the effect that the particles as well as the dissolved BSA are charged negatively. The adsorption of BSA is strongest at low salt concentration and decreases drastically with increasing amounts of added salt. Virtually no adsorption takes place at salt concentrations over 0.1M.[1] The main driving force of the adsorption process is located in a release of numerous counterions of the brush and the protein which increases the entropy of the system.

Experiments by small angle X-ray scattering (SAXS) state that the protein molecules are dispersed within the surface layer of the nanostructured particles.[2] Hence, the SPB present an example for the possible use of nano-structured particles in biotechnology: These particles could be used e.g. for protein separation in solution or as carrier particles for enzymes.

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Poster Presentation Abstracts

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FunSMARTS I — Designing Self-assembled Nanostructures: Metal - Organic Molecule Coordination Networks at Surfaces

Networks of isolated metal atoms and organic ligands can be designed to self-assemble at surfaces in desired patterns, producing regular 2D nanopore lattices, whose dimensions and properties can be controlled by selection of the organic ligand. We constructed such a network by coordination of molecules containing pyridyl groups with the inherent adatom population on a Cu(100) surface at room temperature. We produced the same network on Ag(100) and Ag(111) by depositing Cu atoms with molecules, showing the network rigidity and stability on different substrates due to effect metal-organic coordination. Rectangular networks with higher complexity were formed from two species of organic ligands with metal atom nodes. The nanopore size and aspect ratio can be tuned by independently selecting the two ligand species. Some properties of these designed nanostructures can be 'tuned' by rational selection of the organic molecule and metal components. We have especially explored the adsorption of simple molecules on these networks, which may be of interest for future chemical or catalytic applications. The ability to tailor the size and functionality of nanometer-scale arrays produced by self assembly represents a unique opportunity for molecular recognition, heterogeneous catalysis, and other fields.

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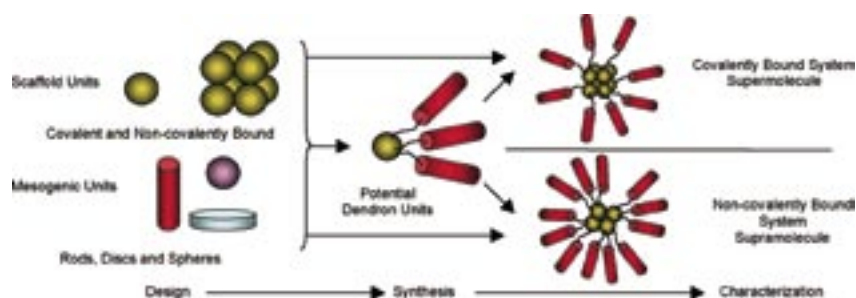
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LC-NANOP — Liquid Crystal Nano-particles

Liquid crystals (LCs) are the quintessential, self-organising, molecular materials of the modern era. The ease with which they can be reoriented in electrical, magnetic and mechanical fields has led to a plethora of applications, resulting, for example, in the dominance of the electro-optic displays market. Most LCs have been designed as either low molar-weight materials for displays (eg 4-alkyl-4'-cyanobiphenyls) or high molecular-weight materials for high yield-strength polymers (eg Kevlar™). In contrast, nano-structured LCs can combine self-organisation with the ability to form secondary and tertiary structures, in a structural hierarchy similar to that found for proteins. Furthermore, super- and supra-molecular LCs can exhibit a variety of physical properties which make them attractive for applications in the fields of nanoscience, materials and biology. We predict that future materials research and applications of LCs will be focused on a variety of exciting topics, which reflect our ability to control self-organising, self-assembling and micro-segregating processes of complex/giant molecular systems to yield addressable, self-organised nanostructures. Materials themselves will be “property designed” and synthesised with smart and often multifunctional characteristics. Their applications will spread across the boundaries from advanced technological devices through to smart bio-materials/sensors, even to the discovery of new “states of matter”. Thus, in this report, we will discuss the rational design, synthesis and characterization of super- and supra-molecular materials with in-built functionalities, which self-organise and/or self-assemble in order to yield novel materials or states of matter of practical importance.

The liquid-crystalline super- or supra-structured materials are designed, with the aid of simulations, in the form of a nano-particle (eg, organic, inorganic, biological etc) as the central scaffold, and where the scaffold may be multilayered. Surrounding the scaffold is a “liquid-crystalline coat”, which may be derived from spherical, disc- or rod-like mesogenic units, see below. The external coat can consist of one or more mesogenic layers, which in turn can accommodate further functional units (eg photochromic).



Thus the objective of the LC-NANOP Network is the design and preparation of LC nano-particulate materials, characterisation of their chemical structures, and determination of their condensed phase structures. In addition we will examine their response to, and behaviour in, applied fields, and their important physico-chemical properties, eg, electro-optic, magneto-optic, electro-mechanic and photonic.

Poster Presentation Abstracts

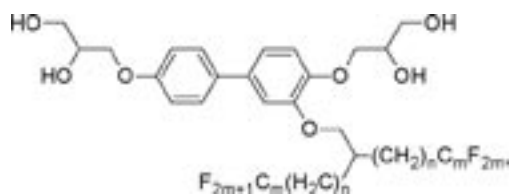
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SCALES — Complex mesophase morphologies of low molecular weight blockmolecules

Low molecular weight block-molecules have become a field of increasing interest in the last years. It was shown that the combination of amphiphilic self-organisation with the driving forces for parallel arrangement provided by rigid segments leads to the formation of exciting novel mesophase structures [1]. Rigid bolaamphiphiles with flexible lateral chains represent one class of such compounds. They can be regarded as low molecular weight block-molecules, in which three incompatible blocks (polar diol groups, rigid aromatic cores, flexible lipophilic chains) are combined. The segregation of these subunits into their own subspaces leads to a wide variety of unique liquid crystalline phases [2].



Herein we report about new mesophase structures obtained from rigid bolaamphiphiles carrying branched lateral chains. These lateral substituents are containing perfluorinated segments which are separated from the rigid core by an aliphatic spacer. The influence of the length of the perfluorinated segments as well as the length of the aliphatic spacer will be discussed. The mesomorphic properties were investigated by polarized light microscopy, differential scanning calorimetry and X-ray diffraction. Whereas the compound with the shortest perfluorinated segment shows exclusively a lamellar mesophase with a triply segregated layer structure, for the compounds with longer perfluorinated chains columnar and two cubic mesophases with different symmetry could be detected at higher temperatures. The formation of this mesophases can be explained by the different thermal expansion of the separated molecular parts with increasing temperature, which leads to a transition from the layer organization via modulated layer structures with columns of the perfluorinated segments in the non-polar sublayers to continuous cubic phases with a core shell morphology.

Acknowledgment: this work was supported by the German Research Council (DFG) and the ESF in the framework of the SONS Eurocores project SCALES.

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SCALES— Three-dimensional Liquid Crystal Structures by Supramolecular Self-Assembly

We investigated the thermotropic liquid crystal behaviour of T-shaped triblock molecules consisting of a rod-like p-terphenyl unit, a laterally attached flexible hydrophilic oligooxyethylene chain terminated with an ionic group, and two end-attached lipophilic alkyl chains. These compounds have been investigated by polarized light microscopy, DSC and X-ray scattering [1-2]. Depending on the length of lipophilic segments, two different kinds of 3-D liquid crystal ("soft crystal") phases were established. Presently we study their structures by reconstructing the electron density maps from XRD data. The 3-D contour maps are shown in Figure 1. The phase shown on the left is rhombohedral (space group $R\bar{3}m$). Here separate polar domains are dispersed within the aromatic layers on an ordered 2D hexagonal lattice, resulting in ABC stacking of layers. In the phase on the right in Figure 1 (space group $P6/mmm$) the polar domains had coalesced across the aliphatic layers, resulting in hexagonally arranged infinite channels penetrating through the stack of alternate aromatic and aliphatic layers. In some compounds phase transition between these two structures can be achieved, either by changing temperature or by adding a polar solvent or changing the cation. Potential application of such structures as thermoreversible or chemically controllable ion channels are being investigated.

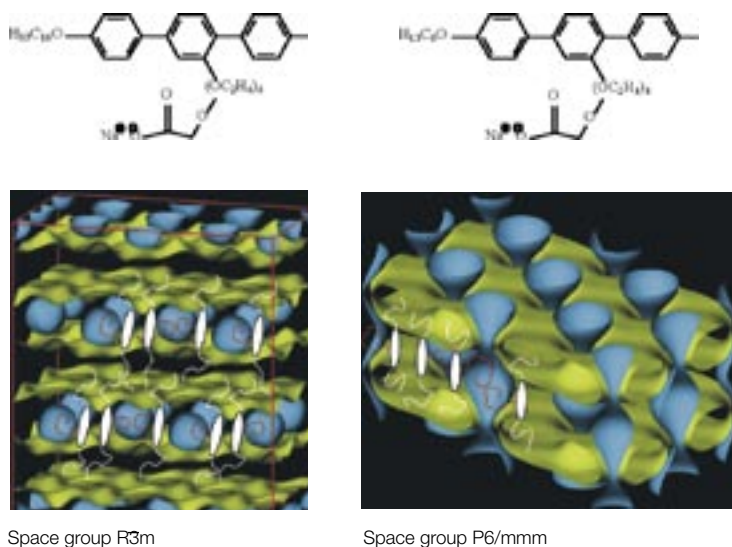


Figure 1. Two-contour electron density maps of the Rhombohedral (left) and the Hexagonal Channeled Layer phase, with several schematic molecules added. The polar regions are marked in blue.

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SOHYD — Self-assembled nanostructured bulk heterojunction devices from multifunctional block copolymers

Morphology and energetic levels play crucial roles in organic semiconducting devices. In organic solar cells, one pivotal parameter is the creation of a large donor-acceptor interface for efficient charge separation[1] while maintaining sufficient contact between same type of molecules for charge transport to the respective electrodes. This can be achieved using block copolymers that phase separate on the nanometer scale and contain at the same time all functionalities for light absorption, charge separation and charge transport required in an organic solar cell[2].

For that purpose we synthesized different block copolymers containing either triphenylamine or dimethoxytriphenylamine units as hole transport material and perylene bisimide moieties as dye and electron transport material by nitroxide mediated controlled radical polymerisation (NMP). (Fig. 1). The NMP was optimised both for the macroinitiator and block copolymer synthesis. The kinetics of polymerisation was studied in order to get good control of molecular weight and low polydispersity. A series of polymers with varying amounts of dye content was obtained for each macroinitiator. All the polymers were characterized using GPC, ¹H-NMR, FTIR and UV-Vis and Fluorescence spectroscopy and the results are compared in this contribution.

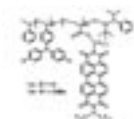


Figure 1. Chemical structures of fully functionalized block copolymers for nanostructured bulk heterojunctions. Block copolymer **1a** contains triphenylamine and **1b** dimethoxytriphenylamine as the hole conducting moieties.

Cyclic voltammetry studies show that the HOMO levels of block copolymers **1a** and **1b** are 5.2 and 5.0 eV, respectively. Both exhibit a LUMO value of 3.60 eV. All block copolymers exhibit microphase separation showing very long wire-like perylene diimide domains with a constant thickness between 13 to 15 nm and lengths of up to several microns (Fig.2).

200 nm 200 nm 200 nm 200 nm

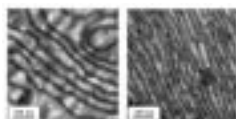


Figure 2. TEM (cross-section) of bulk samples of block copolymers **1a** (left picture) and **1b** (right picture) containing 86 and 72 wt.-% perylene diimide, respectively. Microphase separation occurs throughout the bulk sample where very long perylene diimide wire-like structures are observed.

The similar composition and bulk structure of the two diblock copolymers **1a** and **1b** allowed a direct investigation of the influence of HOMO levels on the photovoltaic characteristics. The charge transfer rate could be maximized by varying the donor HOMO level in a given system[3]. In figure 3, I-V-curves of photovoltaic devices made of **1a** and **1b** are shown. The simplicity of this approach is that a single layer of the multifunctional block copolymer, which self-assembles into a nanostructured bulk heterojunction fulfils a majority of prerequisites for an efficient polymer cell with long term morphological stability.

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SOHYD — Poly(3-AlkylThienylene Vinylene) derivatives: Low band gap p-type conjugated polymers for photovoltaics

Low band gap conjugated polymers stay an intriguing research topic in the context of organic photovoltaics. Indeed such materials, because of their long-wavelength absorption, may improve the optical response of the active layer. As such their use as a component in tandem solar cells, may substantially improve the efficiency of the cell. Poly-3HexylThiophene (P3HT), although at the borderline of being low band gap (< 2 eV), demonstrates the potential of said material class. The performance observed is directly related to the synthetic method used to synthesize P3HT, e.g. the Rieke method. The down side is that toward the synthesis of low band gap conjugated polymers there are not many synthetic routes that yield all specifications on band gap, solubility, stability, molecular weight, etc. Recently for the first time, an efficient synthetic route toward Poly(Thienylene Vinylene) (PTV) derivatives has been developed, more specific the dithiocarbamate route. This new method yields after thermal conversion high molecular weight PTV's (Mw >70 000 Dalton). The procedure allows the synthesis of substituted PTV's, e.g. P(3HexylTV) and P3DodecylTV). The P(3HexylTV) polymer with an optical band gap of 1.7 eV, a HOMO level of -5.1 eV and a LUMO level of -3.1 eV shows a high mobility of charge carriers ($\mu = 10^{-2}$ - 10^{-3} cm²/Vs) and in line with this data, characteristics interesting for photovoltaic applications. Recent results point to the formation of a regioregular structure during polymerization. An overview will be given in this contribution of material characteristics and their performance in photovoltaic devices.

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SUPRAMATES — Solvent vapour annealing: a simple post processing route to achieve long range order in functional materials

The search for simple ways to process organic materials into self-organized functional architectures is of great importance in materials science.[1] Here we describe the enhancement in the degree of order shown on various discotics deposited from solution on SiO₂, as obtained by an annealing step in a controlled solvent vapour atmosphere.[2]

When spun on SiO₂, perylene-bis-dicarboximide (PDI) molecules functionalized with short alkyl chains assemble into needle-like nano-crystals as revealed by Scanning Force Microscopy. Upon exposure of these samples to THF vapours a dramatic increase of the crystal size is attained, with the formation of millimetre-long PDI fibres whose growth complies with nucleation governed growth phenomena described by an Avrami kinetic model.[3] When the same approach is used with other molecules, i.e. PDI or hexabenzocoronene (HBC) derivatives functionalized with long aliphatic residues, needle-like crystals is formed starting from the initial multilayered morphology.

Perylene fibres obtained via THF vapour annealing on transistor source-drain architectures displayed an enhancement of electrical conductance of over one order of magnitude as compared to non-annealed samples. The electronic properties of the different architectures were also investigated by Kelvin Probe Force Microscopy with a nanoscale resolution.[4] Our simple approach combining casting and vapour annealing is cheap and up-scalable, thus of general interest for application in organic nano- and micro-electronics.

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SUPRAMATES — Electric-field patterns around electrodes used for electric-field-assisted alignment of organic supramolecular fibres

We present finite element analysis of the electric-field distribution between and above in-plane electrodes. These electrodes are used for electric-field-assisted alignment of organic supramolecular fibres by dielectrophoretic forces. Supramolecular fibres and other self-assembled structures are particularly promising in the field of organic electronics as they can exhibit improved charge transport properties over randomly oriented analogue structures. However, to make useful supramolecular devices, better control is required over the positioning and orientation of supramolecular objects, which are intrinsically anisotropic. In the electric-field-assisted deposition process, a DC voltage is applied across the electrodes whilst depositing the supramolecular fibres on the electrodes by drop-casting from solution. Electric-field patterns around a number of electrodes of various geometries are presented in order to study how the choice of geometry may affect the positioning and orientation of deposited fibres.

Poster Presentation Abstracts

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SUPRAMATES — Near-Field Lithography of Conjugated Polymer Thin Films

Scanning near-field optical lithography (SNOL) has been shown to provide a versatile method for patterning materials on the nano-scale, well below the classical diffraction limit. We apply this technique to the patterning of thin films of conjugated polymers. These optically and electronically active materials have attracted considerable academic and commercial interest for incorporation into devices such as LEDs and solar cells, since they are chemically tuneable, flexible, and can be processed directly from solution. For applications in photonic devices and nano-electronics, the ability to achieve lithographic resolution on the nano-scale is vital. Using a home-built SNOL system, we demonstrate how conjugated polymer thin films can be patterned to a predetermined and reproducible design. For the commonly used polymer poly(p-phenylene-vinylene) (PPV) we demonstrate reproducible lithographic feature sizes of 85nm, and minimum feature sizes down to 50nm. We also present examples of other functional polymers which are suitable for use with such a technique.

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SUPRAMATES — Perylene diimide multichromophores as single-photon sources

Single-molecule fluorescence spectroscopy was performed on a number of perylene diimide multichromophores (PDI) with different dendritic geometries, [1] with the particular goal of characterizing their performance as single-photon sources at room temperature. [2] The quality of the different PDI-based dendrimers as single-photon source was evaluated by determining the Mandel parameter. We have shown that multichromophoric PDI-based dendrimers (fig 1) behave as single-photon emitters with similar Mandel parameters as for the previously reported perylene monoimide dendrimers (PMI). The main difference with PMI multichromophoric dendrimers, in which triplet formation is a critical limiting factor, is that PDI compounds will perform better in an oxygen-free environment which is important if the compounds are to be incorporated into device-type samples, for example the configuration used in OLED's, since these devices provide nearly oxygen free environments. It was found that working in oxygen free conditions will avoid the formation of long off-times related to the formation of radical ions. These results can be rationalized taking in account the different energy levels of different excited states and the energy transfer between PDI chromophores inside the dendritic structures. Transient femtosecond absorption experiments coupled to molecular modelisation gave further insight in the mechanism responsible for single photon emission of PDI-based dendrimers. Then our next step was to obtain single photon source PDI nanoparticles. Preliminary results will be discussed about different sizes of PDI nanoparticles prepared by laser ablation or poly-condensation.

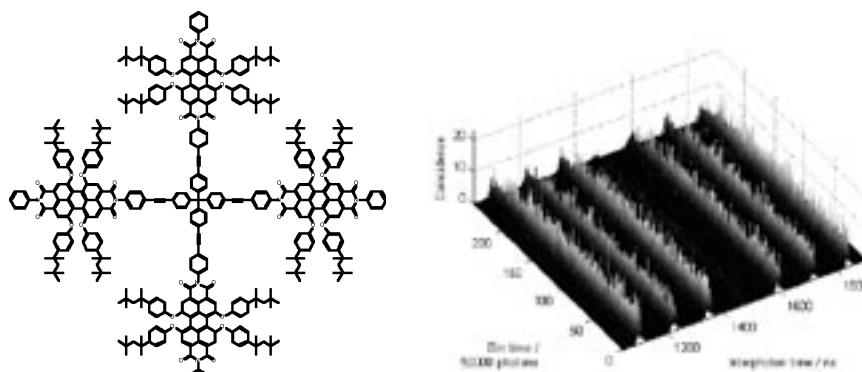


Fig 1: 3D interphoton time histogram for a single molecule of a PDI-based dendrimers studied in PMMA (the absence of peak in the center is a signature of single-photon emissions).

[1] C. Flors, I. Oesterling, T. Schnitzler, E. Fron, G. Schweitzer, M. Sliwa, A. Herrmann, M. Auweraer, F. C. de Schryver, Klaus Müllen and J. Hofkens *J. Phys. Chem. C*, **2007**, 111, 4861-4870

[2] M. Sliwa, C. Flors, I. Oesterling, J. Hotta, K. Müllen, F. C. de Schryver and J. Hofkens *J. Phys.: Condens. Matter.*, **2007**, 19, in press

Poster Presentation Abstracts

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SUPRAMATES — Kelvin Probe Force Microscopy of photovoltaic hetero-junctions: visualizing surface potential at the nanoscale

The photovoltaic performance of bulk hetero-junctions organic solar cells strongly depends on their structure at the nanoscale. In fact, it is notorious that the presence of self-organized nanostructures, phase segregation, defects and domain boundaries influences both charge generation and transport. Thus, techniques capable of measuring electrical properties of the materials at the nanoscale, and to correlate such properties with the morphology, are needed.

Kelvin Probe Force Microscopy (KPFM) [1] is a powerful nanotool to map simultaneously in real-space and real-time the structure and electrical potential of blends upon illumination, as proven by detailed characterization of organic[2] and inorganic[3] materials.

We describe KPFM measurements of photovoltaic blends, composed by polymeric or small self-assembling molecules. Voltage build-up upon illumination is visualized on thin layers of small, isolated nanometric crystals and on nanometric bundles composed by few single-polymer chains. The correlation between charge generation and diffusion in thick and thin layers is discussed, allowing a greater understanding on the processes involved in organic photovoltaic devices on the nanoscale.

[1] V. Palermo et al., Adv. Mat. 2006, 18, 145

[2] V. Palermo et al., Adv. Funct. Mat., 2007, 17, 472; M. Chiesa et al., Nano Lett. 2005, 5, 559

[3] S. Siebentritt et al., Phys. Rev. Lett. 2006, 97, 146601

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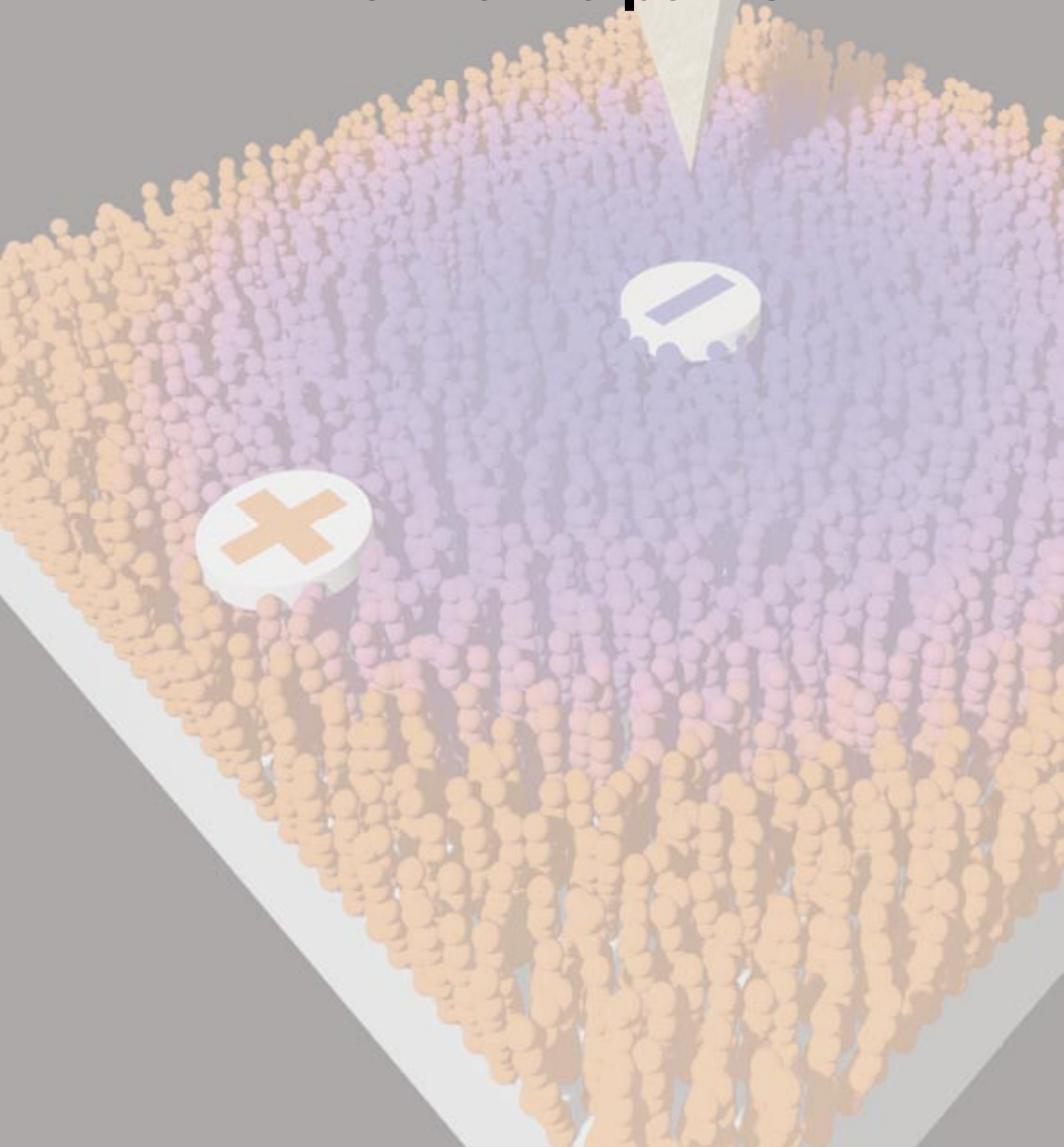
SUPRAMATES — Surface potential measurement of small self-assembled organic nanostructures, and its dependence on nanostructures size and substrate nature

The morphological and electrical characterization of self-organized nanostructures at the nanoscale is fundamental for their application in (opto)electronics devices. The electronic properties of small structures such as nanocrystals, nanowires, nanodots, etc. can be significantly different from the ones of the bulk material, and new behaviours (such as charge quantization, formation of surface dipoles, strong polarization and Fermi level pinning) can appear.[1] In this work, we used KPFM to measure the dependence of surface potential on the dimensions of nanocrystals of perylene-bis-dicarboximide (PDI). KPFM explorations of nanocrystals having different thickness revealed potential variations due to band-bending and Fermi level alignment at the PDI-substrate interface. Space charge regions of hundreds of nm are probed by varying the thickness of the self-assembled PDI structure. We have devised a 3D model to simulate the KPFM results taking into account the contribution of the substrate to the measured potential and the nanostructure polarizability. [2] We propose a method to quantify the surface sensitivity of the technique in order to estimate the effective volume of the sample interacting with the tip. These results are of importance as they make it possible to gain a quantitative determination of electronic properties such as band-bending and local surface potential of hetero-structures, towards the optimisation of the electronic properties of organic (nano)electronic devices.

[1] V. Palermo et al., *Adv. Materials* **2006**, 18, 145.

[2] A. Liscio et al., *Adv. Funct. Mater.* **2006**, 16, 1407.

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