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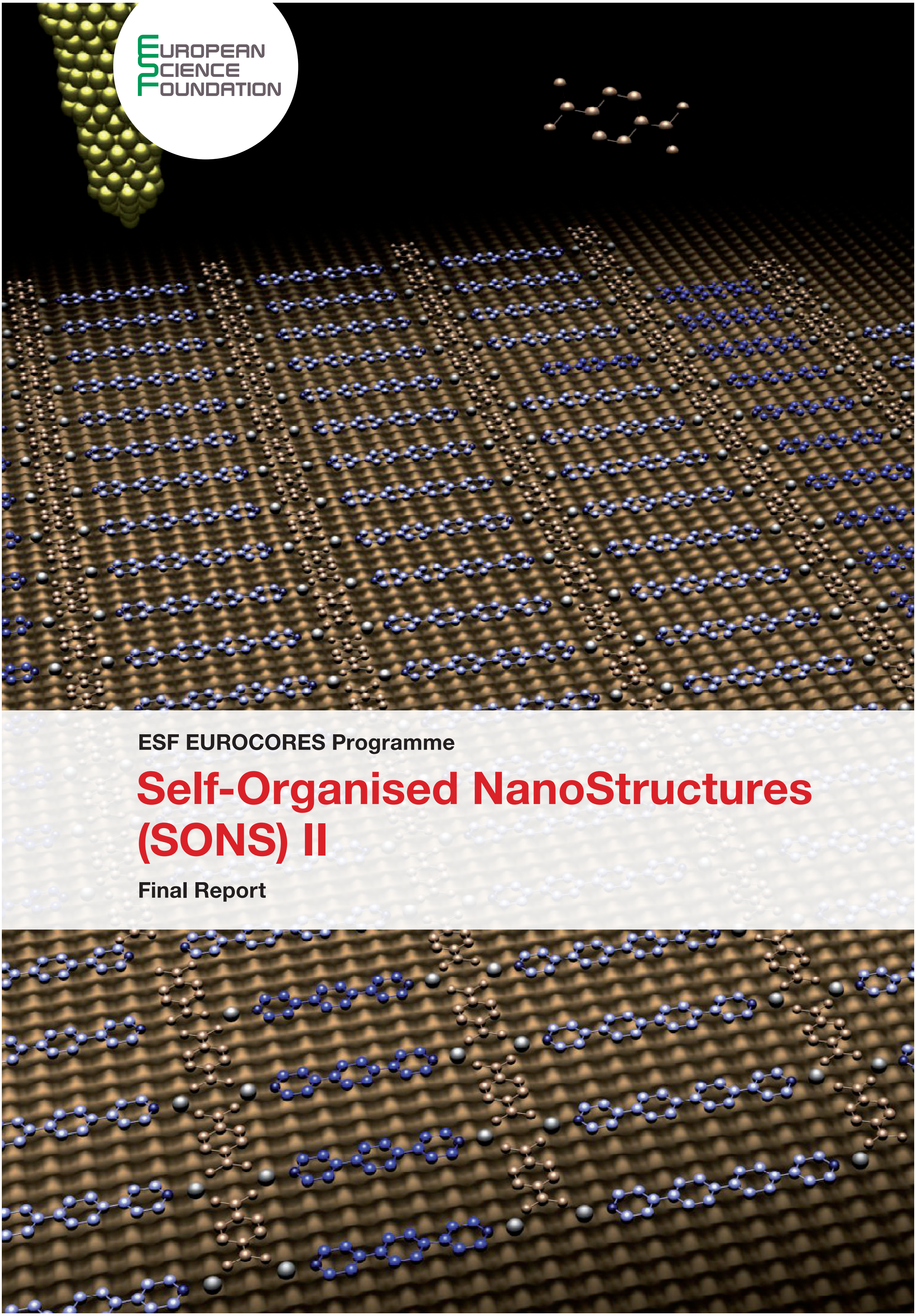

ESF EUROCORES Programme

Self-Organised NanoStructures (SONS) II

Final Report

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Cover picture:
Nanometer scale organisation of molecular components on a copper surface, demonstrating sorting of two sizes of molecules (in dark and light blue) through active molecular self-selection. Professor M. Ruben, Research Centre Karlsruhe, Germany, (Fun-SMARTs II Project). © KIT/MPG

EUROCORES
(European Collaborative Research)

The European Collaborative Research (EUROCORES) Scheme enables researchers in different European countries to develop collaboration and scientific synergy in areas where international scale and scope are required for top class science in a global context.
The scheme provides a flexible framework for national basic research funding and performing organisations to join forces in supporting forefront European research in and across all scientific areas.
Until the end of 2008, scientific coordination and networking was funded through the EC FP6 Programme, under contract no. ERASCT- 2003-980409. As of 2009, the national organisations support all aspects including scientific coordination, networking and research funding.

www.esf.org/sons2

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Foreword

Self-Organised NanoStructures (SONS) was the first EUROCORES programme to be launched at the ESF in the area of physical and engineering sciences back in 2002, recognising the need for basic research in the cross-disciplinary science of self-organisation at the nanoscale. This first call resulted in 16 Collaborative Research Projects (CRPs) and a second, more focused call was launched in 2005 with seven CRPs funded for the period 2006–2010. The goal of SONS II was to generate fundamental knowledge about interactions governing self-organisation (or self-assembly) processes in complex systems such as supramolecules and nanostructures. This rapidly growing field, highlighted in many countries as extremely important in science and technology, opened the way to cross-disciplinary collaboration between physicists, materials scientists, chemists and biologists.

Over the course of SONS, significant scientific achievements have been made by the synergistic efforts of the CRPs, resulting in the development of common tools and producing many high-level publications. Through its conferences and joint workshops, SONS fostered innovative and multidisciplinary collaborations among the project investigators and their laboratories. New research lines were developed, tools and know-how exchanged, and young postdoctoral and PhD students had the opportunity to present their research to leaders in the field.

The collaborations that have been established will hopefully continue and strengthen, and hence contribute to the wider international effort addressing the many remaining questions and challenges in this exciting field.

With this we would like to thank the project leaders and all scientists and ESF colleagues involved for their high-level contribution and commitment.

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Head of Unit, Physical, Engineering
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Dr Ana Helman
Science Officer

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*Fonds zur Förderung der wissenschaftlichen Forschung (FWF) / Austrian Science Fund**

Belgium
*Fonds voor Wetenschappelijk Onderzoek – Vlaanderen (FWO) / Research Foundation Flanders**

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Germany
Deutsche Forschungsgemeinschaft (DFG)/ German Research Foundation

Italy
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Poland
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2.
Description of the SONS II Programme

2.1 Background and Rationale

Complex organic molecules, supramolecular assemblies, tailor-made polymers and inorganic nanoparticles attract widespread attention in contemporary chemistry, physics and materials science. This attraction originates from a continuing interest in miniaturisation of functions, and from the opportunities that arise for applying such novel molecular materials in new and technologically advanced applications from the "top-down", e.g. in electronics and photonics. Such molecular architectures also present the basis for a "bottom-up" approach in nanotechnology.

Self-organisation is a process in which a supramolecular organisation is established in a complex system of interlocking components. The mechanism that produces the organisation is determined by the competing interactions between the components. The hierarchy of interactions determines the hierarchy of levels in the final nanostructured material. As a result, self-organising compounds allow a defined and well-controlled construction of ordered architectures on a nanometre scale. Systems, for instance self-assembled monolayers and template-directed polymers, which have been created by self-assembly methods can also be structured, for example by using nanolithography, so that a further arrangement of these functional architectures on a mesoscopic lengthscale, and thus the engineering of novel materials, is possible.

The SONS II EUROCORES programme concerned the utilisation of supramolecular interactions for the synthesis and positioning of functional assemblies, macromolecules, dendrimers, liquid crystals, tailor-made polymers and inorganic nanoparticles. Ultimately molecular self-assembled architectures may find applications in advanced technologies such as new chip technologies (DNA probes, lab-on-a chip), sensors, transistors, data storage, light-emitting diodes, communication technologies, magnetic information storage, photovoltaic cells, and molecular motors and machines. Therefore over the past few decades techniques for directing the assembly of molecules have been intensively pursued. On the molecular scale these include ionic interactions, metal–ligand interactions, and hydrogen- and p-bonded complexes. At a higher hierarchical level assembly occurs by means of the complementary and antagonistic interactions present in liquid crystalline mesophases and phase-separated block copolymers. Indeed researchers can now design materials that assemble themselves into complex, finished structures.

Self-assembly is an example of a subject in which both engineering development and the resolution of fundamental scientific problems are essential for realising the full potential that SONS offer. For this reason, by bringing together expertise from a range of backgrounds and countries, the programme aimed to develop cross-disciplinary SONS research at the interface between chemistry, materials science, nanoscience, physics and engineering.

2.2 Scientific Themes and Research Objectives

The processes observed in nature in which nanostructures are built up through the self-assembly of molecules are very attractive. Theoretical methods and high quality simulations will aid in understanding the characteristics of this behaviour, which should in turn lead to advances in the laboratory. In addition, it seems logical that the extension to larger dimensions will benefit from using the principles and methodologies of nature, first for the preparation of small synthetic objects and machines via self-assembly. Central to this construction process is the development of simple chemical systems capable of self-organising into nanometre-sized structures through mutual recognition properties.

In SONS II particular attention was given to molecular self-assembly, focusing on soft and/or supra-molecular matter in connection with mechanisms, functions and fabrication of SONS. For this type of research a strong interdisciplinary combination of organic, macromolecular, polymer, supramolecular and inorganic chemistry; physics; engineering from nano- to mesoscopic length-scales; and theoretical modelling is required. This includes the design and synthesis of nano-sized objects, such as dendrimers, fullerenes, metallic or semiconducting nanoparticles, proteins, polymers, block copolymers, hybrid systems and nanomagnets. The intention should be to synthesise, in a simple and possibly rational way, supramolecular assemblies that are able to interact on a higher hierarchical level. With such a modular system it is possible to take up the challenge of constructing and studying molecular assemblies of increasing complexity capable of performing increasingly more complex functions.

Via the combination of self-assembly with modern micro- and nano-engineering processes these synthetic nano-assemblies must be connected to the outside world. Consequently creating links that connect the molecular scale to the macroscopic world was one of the focal points of the programme.

2.3 Description of the Collaborating Research Areas

The areas of research included in the SONS II EUROCORES programme are set out below in an account of the call for proposals.

2.3.1 Materials nanostructured by self-organisation

Nanostructured materials are considered to be at the crossroads of molecular and bulk dimensions. Such materials may consist of combinations of molecular systems, polymers (synthetic and biomolecule-based), inorganic semiconductors, nanogels, metals, and colloidal particles, and can be constructed by the use of self-organising properties. In this emerging field of research, in which nanoscopic dimensions become crucial for macroscopic (e.g. electric, photonic, catalytic) properties, synthetic organic, supramolecular, and polymer chemistry can be combined to create functional nanostructures and nano-assemblies. Ultimately, understanding and control at different length scales and interfaces is required to reach the intrinsic limits of such nanostructured materials. The design, synthesis and analysis of complex block copolymers and other molecular systems with specific molecular interactions can be used to create these nanostructured materials. This also provides the opportunity to introduce more than one characteristic length scale in one self-assembly process. Self-regulation and self-replication are novel extensions to self-assembly in this respect.

2.3.2 Synthesis of 1-, 2- and 3-dimensional nano-objects

Nano-objects which extend into one, two, or three dimensions (e.g. stacks, self-assembled monolayers, nanocrystals) in a 1–100 nm range can serve as building blocks at a higher hierarchical level. The rational preparation of such nano-objects, especially when involving recognition sites or surfaces for further functionalisation via inorganic and organic synthesis, supramolecular self-assembly techniques, and polymerisation procedures is a scientific challenge. The creation of such well-defined molecular objects is required for the construction of extended ordered functional architectures as well as devices. To build these nano-objects the whole range of supramolecular assemblies (for example metal complexes, dendrimers, phorphyrins, fullerenes, and so forth), metallic (dots, rods, and wires) or semiconductive colloids (nanoparticles), or biological systems can be employed. In addition, it is of interest to control the self-assembly phenomena (of both molecular and colloidal systems) via external stimuli such as light, electrical or magnetic fields.

2.3.3 Hierarchical self-assembly

This sub-field connects the self-assembly and self-recognising processes with nano- and microstructuring methods. The ordered arrangement of functional molecules and functional nano-objects or biomolecules (e.g. proteins, oligonucleotides, fibres) at predefined positions of nanopatterned substrates offers new possibilities for materials and devices, such as photonic crystals, molecular lasers, data storage and sensors. Hierarchical self-assembly remains one of the most intriguing methods to accomplish these goals, and increases the complexity of the objects which are synthesised from the bottom up. The desired diversity and functionality require the ability to use nanostructuring techniques, for example scanning probe techniques, nanoimprinting, nanolithography, microcontact printing and embossing, to create complex nanopatterned substrates and nano-objects with specifically designed functionalisation patterns.

2.3.4 Theoretical methods and simulation

In addition to experimental work, theoretical methods, electronic structure calculations and high quality simulations, for example, are necessary to gain more insight into self-assembly processes. There is a clear need to understand when self-assembly is driven by energy, i.e. when the resulting structure is a thermodynamically stable (or metastable) phase, and when it is driven by kinetics. In fact, many biological objects are a result of the nonlinear behaviour in an open system, and these structures are then 'frozen in'. It is very useful to obtain a deeper understanding of the complex balance of the many intermolecular interactions with different physical and chemical origin, and the role of statistical mechanics during the self-assembly process.

2.3.5 Molecular positioning

This area of the programme includes the development and implementation of new characterisation and directed positioning techniques for nanoscale objects and molecules. Modern scanning probe microscopy (SPM) methods – atomic force microscopy (AFM), scanning tunnelling microscopy (STM), scanning near-field optical microscopy (SNOM) – offer an outstanding possibility in this respect for the visualisation and positioning of single molecules and nanometre-sized objects. In addition, combined techniques for the selective activation of controlled chemical reactions by the SPM tip (scanning probe controlled chemistry), and selective methods for nanostructuring and nanoprobing of chemical, physical (e.g. switching molecular states) and biological properties have been tackled. Furthermore SPM methods may be employed to construct templates (e.g. via positioning of molecular units or ordering of surfaces) to be used in the context of the other sub-fields described.

2.3.6 Molecular and supramolecular electronics and motors

The dimensional limit of molecular materials in electronic and optical applications can be achieved when it is possible to address individual molecules or small clusters thereof in a predefined way. Presently, various "molecular machines" and "devices" have been described in the literature. In most cases such devices are not addressed individually, or they consist of a single or a few isolated molecules; the functional interconnection of such devices has rarely been achieved. The major challenge for molecular devices in the near future is to find ways to build integrated circuits by bottom-up integration from the molecular level. Therefore one of the goals in this field is to design and construct well-shaped and chemically stable electrical contacts for nanoscopic molecular devices. Ultimately this will involve electrodes of the same dimensions as the molecular components. It is well known, however, that the electronic and chemical properties of small metal (nano) particles are different from those of bulk metal. Furthermore, the desired physical properties of nanoscale systems are a composite function of one or more functional molecules in contact with the functional support and interface. Research shall shed some light on size, dimensionality, surface and interface effects of such properties which may affect the function and design of future nanoscale devices. In addition to electrical properties, mechanical and electromechanical properties of molecular systems, i.e. molecular motors propelled by chemical, optical, or electrical energy, are emerging and of interest. Specific challenges here concern the coupling of rotations and translations as well as inducing coherent behaviour and the positioning of such systems on surfaces.

2.3.7 (Opto)electronic properties of self-assemblies

Studying, understanding, and controlling the (opto) electronic properties of molecular self-assembled systems is a crucial part of research in this field. Progress in nanotechnology has shown that it is possible to contact individual molecules and create nanoscale electronic devices. The nanometre length scale dictates that mesoscopic, semiconductor and molecular physics must be combined to understand transport properties in, for example, molecular field-effect transistors and (supra)molecular wires. Single molecule devices allow the investigation of many fundamental properties; as an example the mechanisms of charge transport in single molecule devices through coherent tunnelling or vibronic transport are of fundamental interest and need to be investigated. With respect to optical properties it should be noted that optical microscopy techniques for thin film analysis are undergoing a revolution to meet the challenges of analysing complex systems. Recent developments in optical and confocal microscopy and SPM, such as NSOM, provide optical information about single objects on the nanometre-scale. In combination with transient spectroscopies both spatial and temporal information of the molecular self-assemblies can be gained. Molecular scale electronic and optic circuitry goes far beyond the miniaturisation of existing electronic devices. These concepts offer the possibilities to introduce new functionalities which are at present limited by our imagination.

2.3.8 Self-assembled nanomagnets

The magnetic interactions among nanomagnets determine processes such as the self-organisation of magnetic moments to minimise the local field at each nanomagnet, or the self-ordering of particles into chains with a given symmetry. In some cases, self-assembly processes lead to particular nanomagnet arrays, which present characteristics typical of complexity. Improved preparation techniques now allow the accurate control of size and intermagnet distance of (i) nanoparticles monodispersed in ferrofluids or deposited in substrates forming monolayers or heterostructures, and (ii) arrays of electroplated or nanolithographed nanowires. Other controlled deposition processes direct substituents into highly ordered superlattices. All these self-assemblies provide unique experimental information to elucidate intermagnetic interactions critical for the optimisation of emerging magnetic information storage, and biomagnetic and drug delivery nanotechnologies.

Facts and Figures

Deadline for Applications: 23 June 2005

Funded Collaborative Research Projects (CRPs): Seven consisting of 39 individual research projects in nine different countries.

Duration of Programme:
December 2006 – June 2010

Budget for research: 7.3 M€

2.4 List of Projects

After the international peer review process carefully managed by the ESF, seven CRPs were launched in 2006. These seven CRPs consisted of 39 individual research projects based in nine different European countries.

SUPRAmolecular MATerials for new functional StructurES (SUPRAMATES)

Principal Investigators

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Assembly and Manipulation of Functional Supramolecular Nanostructures at Surfaces (FunSMARTs II)

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Self-Organised Hybrid Devices (SOHYD)

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Liquid Crystals Nano-particles (LC-NANOP)

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Complexity Across Lengthscales in Soft Matter (SCALES)

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Biofunctional Self-Organised Nanostructures of Ionic/Non-ionic Amphiphilic Copolymers, Biopolymers-Biomacromolecules and Nanoparticles: From Bioinspired to Biointegrated Systems (BIOSONS)

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Self-assembled Nanoscale Magnetic Networks (SANMAG)

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2.5 EUROCORES Acknowledgements

To promote the EUROCORES Programme and the national funding organisations who support it (and prior to 2008, the European Commission), all publications, posters, websites and other dissemination outputs are required to be clearly identified as being programme-funded or co-funded. This is an important indicator for monitoring the output of the programmes, particularly in peer-reviewed publications.

For SONS II the acknowledgement until 2008 was:
The European Science Foundation (ESF) provides scientific coordination and support for networking activities of funded scientists currently through the EC FP6 Programme, under contract no. ERAS-CT-2003-980409. Research funding is provided

by participating organisations. SONS II is managed by the Physical and Engineering Sciences Committee (PESC) at the ESF.

From 2009 onwards the acknowledgement is: *The aim of the European Collaborative Research (EUROCORES) Scheme is to enable researchers in different European countries to develop collaboration and scientific synergy in areas where European scale and scope are required to reach the critical mass necessary for top class science in a global context.*

The scheme provides a flexible framework which allows national basic research funding and performing organisations to join forces to support excellent European research in and across all scientific areas.

Until the end of 2008, scientific coordination and networking was funded through the EC FP6 Programme, under contract no. ERAS-CT-2003-980409. As of 2009, the National Funding Organisations will provide the funding for the scientific coordination and networking in addition to the research funding.

3.

Highlights of the Collaborative Research Projects

3.1 SUPRAmolecular MATerials for new functional StructurES (SUPRAMATES)

Principal Investigators

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Franco Cacialli
Richard H. Friend
Johan Hofkens
Klaus Müllen

Associated Partner

Alan Edward Rowan

Funding Organisations

Belgium: *Research Foundation Flanders*
Germany: *German Research Foundation*
Italy: *National Research Council*
United Kingdom: *Engineering and Physical Sciences Research Council*

The SUPRAMATES CRP worked towards combining supramolecular chemistry of multifunctional systems with tailor-made nanostructured interfaces to solid substrates and electrodes for applications in organic and plastic opto-electronics. The aim of SUPRAMATES was to achieve a high level of control over different physico-chemical properties (i.e. mechanical, electrical and photophysical) of the materials used for fabricating optoelectronic devices. The activity involved the design and synthesis of molecular modules given the targeted physico-chemical property, and ultimately towards the device to be fabricated. In terms of device fabrication and optimisation, particular attention was given to field-effect transistors (FETs), light-emitting diodes and photovoltaic cells.

The different disciplines included synthesis of new supramolecular components with programmed functions and semiconducting properties, hierarchical self-assembly at surfaces of supramolecular nanostructures across multiple length scales, time- and scale-dependent characterisation at surfaces by single molecule spectroscopy and scanning probe microscopies, nanofabrication of metallic and plastic nanoelectrodes, multi-scale spectroscopic and optoelectronic characterisation of hybrid structures, and fabrication of optoelectronic devices. The complementary expertise and facilities available among the teams made it possible to investigate a variety of physico-chemical properties making use of state-of-the-art approaches such as time-resolved optical characterisation techniques, including SNOM, AFM, STM, KPFM, C-AFM, electroabsorption, STED, PALM. In particular:

- The interaction of the CNR-BO, UCL, UCAM, KUL and ISIS-ULP projects with the two synthetic domains (MPIP and RUN) engaged in the preliminary design of the system to be synthesised with regard to the desired physico-chemical properties and functions of interest. Following the synthesis of the first derivatives and their thorough characterisation, a step-wise approach was used that aimed at the synthesis of new derivatives with optimal properties.
- Among the CNR-BO, UCL, UCAM, KUL and ISIS-ULP projects the joint experiments aimed at exploiting the different methodologies available in the different labs. For example, CNR-BO and ISIS-ULP developed new samples using novel processing and post-processing self-assembly techniques which were then sent to UCAM for testing of the device performance (FETs in particular).

The most innovative research carried out within SUPRAMATES involved all six individual projects. It was devoted to the careful and pre-programmed control over the inter-chromophore interactions making use of macromolecular scaffolds based on ultra-rigid poly-isocyanide polymers exposing optically and/or electrically active moieties in the peripheral positions. Such a multi-chromophoric array was synthesised in different derivatives each exposing a well-defined functional group such as perylene dyes, carbazoles and porphyrins. The research on this new class of systems was focused on:

- the single-molecule study of the properties of individual polymers embedded in a viscous optically inert polymer matrix;
- the fabrication of FETs using as an electroactive layer both monocomponent and bi-component films;
- the realisation of solar cell prototypes and thorough nanoscale-resolved exploration of the photovoltaic activity in bi-component films.

Work within the CRP provided a detailed understanding of the structural, mechanical, optical, electrical and electronic properties of multichromophoric arrays based on ultrastiff polysicocyanodipeptide chains exposing perylene dyes in the lateral positions. Such a scaffolding approach made it possible to achieve full control over the position and orientation of functional units in view of the expected self-assembly behaviour, in particular to tune the interchromophore interaction. It also gave rise to the improvement of the processability of thin films. For this, specific effort was devoted to the development of new processing and post processing procedures including zone-casting, soft-landing, dip-coating, spray-deposition, scanning near-field optical microscopy assisted lithography, and (temperature-enhanced) solvent vapour annealing to control the molecular assembly across multiple length scales, from the sub-nanometre scale up to the macroscopic scale. It was demonstrated that a supramolecular approach over the film formation is key to obtain enhanced characteristics in devices.

The CRP greatly succeeded in combining the supramolecular chemistry of multifunctional systems and the nanostructure of interfaces. New materials have been developed and their properties studied using a great diversity of techniques available in the CRP. The knowledge acquired in SUPRAMATES is believed to be of importance for the optimisation of macroscopic devices such as solar cells, FETs and light-emitting diodes. In addition, the proposed scaffolding approach is of general applicability and interest in the design of building blocks for technologically important functional materials and the potential applicability of supramolecular nanostructures may span from robotics (for artificial muscles), to (bio)materials science. The use of single supramolecules as electro-active building blocks can be expected to pave the way towards inexpensive products with new sets of properties tailored at the single molecule level.

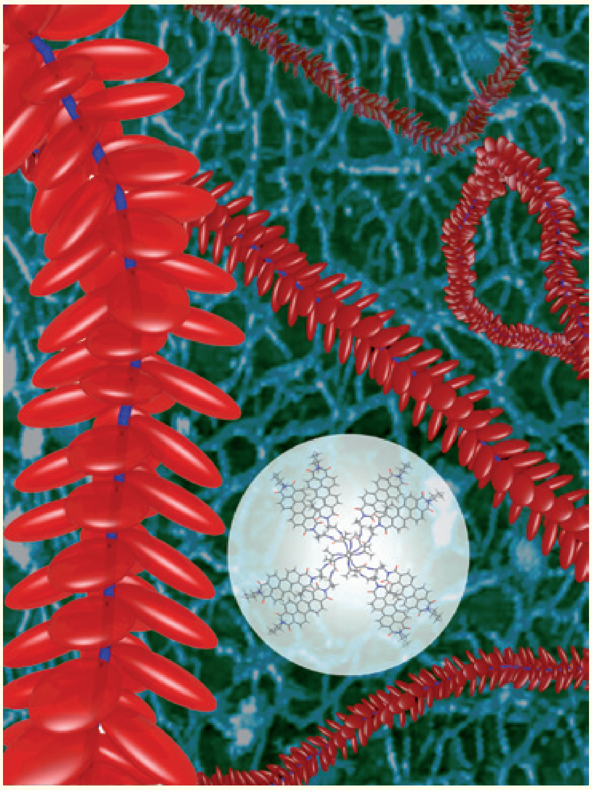

Figure 1.
Three-dimensional representation of a new class of macromolecules for organic electronics formed by rigid polymeric backbones (blue) side-functionalised with thousands of polyaromatic, optically active molecules (red). In the background, the real polymer fibres as presented are visualised by AFM. Palermo, V., Schwartz, E., Finlayson, C. E., Liscio, A., Otten, M. B. J.,Trapani, S., Müllen K., Beljonne, D., Friend, R. H., Nolte, R. J. M., Rowan, A. E. and Samorì, P. Macromolecular Scaffolding: The Relationship Between Nanoscale Architecture and Function in Multichromophoric Arrays for Organic Electronics. *Adv. Mater.* (2010) **22**, E81. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Selected publications

Dabirian, R., Feng, X., Ortolani, L., Liscio, A., Morandi, V., Müllen, K., Samorì, P. and Palermo, V. Micron-sized [6,6]-phenyl C61 butyric acid methyl ester crystals grown by dip coating in solvent vapour atmosphere: interfaces for organic photovoltaics. Phys. Chem. Chem. Phys. **12**, 4473 (2010).

Dabirian, R., Palermo, V., Liscio, A., Schwartz, E., Otten, M. B. J., Finlayson, C. E., Treossi, E., Friend, R. H., Calestani, G., Müllen, K., Nolte, R. J. M., Rowan, A. E. and Samorì, P. The relationship between nanoscale architecture and charge transport in conjugated nanocrystals bridged by multi-chromophoric polymers. *J. Am. Chem. Soc.* **131**, 705 (2009).

De Luca, G., Pisula W., Credgington, D., Treossi, E., Fenwick, O., Lazzerini, G. M., Dabirian, R., Liscio, A., Palermo, V., Müllen, K., Cacialli, F. and Samorì, P. Non-conventional processing and post-processing methods for the nanostructuring of conjugated materials for organic electronics. Adv. Funct. Mater. 21, 1206 (2011).

Finlayson, C. E., Friend, R. H., Otten, M. B. J., Schwartz, E., Cornelissen, J. J. L. M., Nolte, R. J. M, Rowan, A. E., Samori, P., Palermo, V., Liscio, A., Peneva, K,. Müllen, K., Trapani, S. and Beljonne, D. Electronic transport properties of ensembles of perylene-substituted poly-isocyanopeptide arrays. *Adv. Funct. Mater.* **18**, 3947 (2008).

Palermo, V., Otten, M. B. J., Liscio, A., Schwartz, E., de Witte, P. A. J., Castriciano, M. A., Wienk, M. M., Nolde, F., De Luca, G., Cornelissen, J. J. L. M., Janssen, R. A. J., Müllen, K., Rowan, A. E., Nolte, R. J. M. and Samorì, P. The relationship between nanoscale architecture and function in photovoltaic multichromophoric arrays as visualized by Kelvin probe force microscopy. *J. Am. Chem. Soc.* **130**, 14605 (2008).

Palermo, V., Schwartz, E., Finlayson, C. E., Liscio, A., Otten, M. B. J., Trapani, S., Müllen, K., Beljonne, D., Friend, R. H., Nolte, R. J. M., Rowan, A. E. and Samorì, P. Macromolecular scaffolding: The relationship between nanoscale architecture and function in multichromophoric arrays for organic electronics. Adv. Mater. 22, E81 (2010).

Palermo, V., Schwartz, E., Liscio, A., Otten, M. B. J., Müllen, K., Nolte, R. J. M., Rowan, A. E. and Samorì, P. Influence of π-π stacking on the self-assembly and coiling of multi-chromophoric polymers based on perylenebis(dicarboximides): an AFM study. Soft Matter **5**, 4680 (2009).

Petrozza, A., Brovelli, S., Michels, J. J., Anderson, H. L., Friend, R. H., Silva, C. and Cacialli, F. Control of rapid formation of interchain excited states in sugar-threaded supramolecular wires. *Adv. Mater.* **20**, 3218 (2008).

Treossi, E., Liscio, A.., Feng, X., Palermo, V., Müllen, K. and Samorì, P. Temperature-enhanced solvent vapor annealing of a *C3* symmetric hexa-*peri*-hexabenzocoronene: controlling the self-assembly from nano- to macro-scale, *Small* **5**, 112 (2009).

Wöll, D., Uji-I, H., Schnitzler, T., Hotta, J., Deceker, P., Hermann, A., De Schryver, F., Müllen, K. and Hofkens J. Radical polymerization tracked by single molecule spectroscopy. *Angew. Chem. Int. Ed.* **47**, 783 (2008).

3.2 Assembly and Manipulation of Functional Supramolecular Nanostructures at Surfaces (FunSMARTs II)

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Funding Organisations

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Italy: *National Research Council*
Spain: *Interministerial Committee on Science and Technology*
Switzerland: *Swiss National Science Foundation*

The FunSMARTs II CRP was designed to investigate the hierarchical steering of supramolecular self-organisation using complex molecules at well-defined substrates for the fabrication of fully integrated and connected functional nanostructures. It had a strong multidisciplinary character because it comprised synthetic chemistry, physical nanoscience and computational modelling; the experimental work alone brought together scientists with expertise in molecular synthesis, surface characterisation, surface patterning, surface structuring, analytical techniques, and physical measurements.

The primary interest was in molecular magnetism and the research teams used appropriately designed molecular building blocks for the modular construction of functional architectures and nanostructures from organic species and metal atoms at surfaces. The supramolecular self-organisation approach enabled a high degree of structural organisation within the nanoregime and made use of different non-covalent interactions (metal coordination, hydrogen bonding and donor–acceptor interactions). These were directly characterised at the single-molecule level by means of scanning tunnelling microscopy (STM) techniques.

The CRP created a high level of scientific collaboration and work that was carried out within it is at the forefront of research addressed towards the preparation and study of functional supramolecular nanostructures at surfaces. The scientific output of FunSMARTs II includes:

- direct proof and analysis for conformational adaptation in adsorption of flexible species and supramolecular assembly on surfaces;
- realisation of metal–organic honeycomb nanomeshes with tuneable cavity size, along with a detailed understanding of three-fold coordination motifs on metal substrates;
- demonstration of complex networks (chiral kagomé lattice) by self-assembly of ditopic tectons in two dimensions;
- several self-assembled monolayers containing organic radicals have been grafted on surfaces of different nature – Au, Si, SiO_2, HOPG – providing a new way to prepare multifunctional surfaces that combine magnetic, electroactive and optical properties and show switching capabilities;
- structuring a fluorophoric mercury (II) detecting molecule on cellulose fibres and subsequent preparation of a novel functional nanocomposite membrane for the selective detection – down to the ppb level – of this highly toxic metal in water.

One particularly important result centres on the control of magnetic anisotropy which is a key issue in the development of metal–organic materials for magnetic applications. In a joint investigation involving several groups of the FunSMARTs II CRP together with research groups from the SANMAG CRP, the magnetic properties of the recently developed self-assembled metallosupramolecular networks at surfaces were addressed. While Fe atoms adsorbed on Cu(100) constitute a metallic system due to the substantial interaction with the Cu bands, the experiments and theoretical modelling show that Fe–Cu hybridisation is drastically weakened by square-planar coordination to 1,4-benzenedicarboxylic acid molecules. The metal atoms exhibit a high-spin configuration, the magnetic anisotropy of which can be manipulated via lateral and axial molecular ligands. The results provide valuable information for the understanding and control of magnetic properties of metal–organic complexes at the interface with a metal substrate. This constitutes a necessary step towards the implementation of molecular materials into heterogeneous magnetoelectronic devices.

Another highlight is the full spatial structural elucidation of disordered coordination architectures that was achieved using STM directly probing the pertaining molecular-level arrangements. The results revealed the divergent assembly of random string networks on planar surfaces using a prochi-

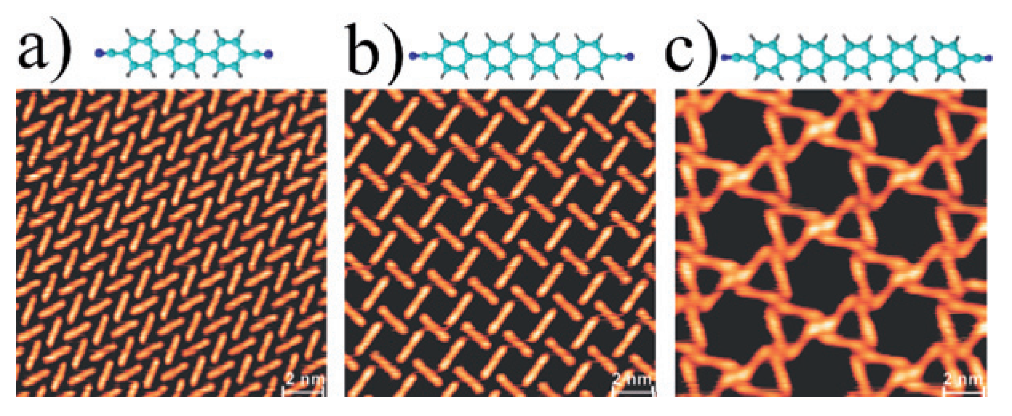

Figure 2.
A surface confined supramolecular organisation of simple linear aromatic molecules, p-NC-Phx-p-CN, leads to a fascinating variety of open networks from a, densely packed chevron layer, x = 3, via b, open rhombic network, x = 4, to c, Kagomé lattice, x = 6. Structure models of molecular building blocks are depicted above the STM images. Their respective lengths are 1.66, 2.09, 2.53 nm (light blue, C; dark blue, N; gray, H). Reprinted with permission from Schlickum, U. *et al. J. Am. Chem. Soc.* **130**, 11778 (2008). Copyright 2008, 2009 American Chemical Society.

ral ditopic linker forming metal–ligand bonds with cobalt centres. The use of coordination interactions renders robust disordered network structures incorporating distinct bifurcation and string motifs based on a scenario mediated by reversible metal–ligand interactions. The connection between molecular symmetry, on-surface metal–ligand interactions and energetic similarity of the predominant three- and fourfold coordination nodes provides design criteria for the engineering of disordered two-dimensional solids. The findings suggest that string networks with randomisation and multiple coordination motifs present a novel route towards a distinct class of robust, adaptive compounds and network topologies situated between so-called metal–organic frameworks and covalent polymers.

Selected publications

Cavallini, M., Facchini, M., Albonetti, C. and Biscarini, F. Single molecule magnets: from thin films to nano-patterns. *Phys. Chem. Chem. Phys.* **10**, 784 (2008).

Díez-Gil, C., Martínez, R., Ratera, I., Tárraga, A., Molina, P. and Veciana, J. Nanocomposite membrane as highly selective and sensitive mercury(II) detectors. *J. Mater. Chem.* **18**, 1997 (2008).

Gambardella, P., Stepanow, S., Dmitriev, A., Honolka, J., de Groot, F., Lingenfelder, M., Gupta, S. S., Sarma, D. D., Bencok, P., Stanescu, S., Clair, S., Pons, S., Lin, N., Seitsonen, A. P., Brune, H., Barth, J. V and Kern, K. Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface. *Nature Mater.* **8**, 189 (2009).

Kühne, D., Klappenberger, F., Decker, R., Schlickum, U., Brune, H., Klyatskaya, S., Ruben M. and Barth, J. V. High quality 2D metal–organic coordination network providing giant cavities within mesoscale domains. *J. Am. Chem. Soc.* **131**, 3881 (2009).

Marschall, M., Reichert, J., Weber-Bargioni, A., Seufert, K., Auwärter, W., Klyatskaya, S., Zoppellaro, G., Ruben M. and Barth, J. V. Random two-dimensional string networks based on divergent coordination assembly. *Nature Chem.* **2**, 131 (2010).

Mas-Torrent, M., Crivillers, N., Mugnaini, V., Ratera, I., Ratera, C. and Veciana, J. Organic radicals on surfaces: towards molecular spintronics. *J. Mater. Chem.* **19**, 1691 (2010).

Schlickum, U., Decker, R., Klappenberger, F., Zoppellaro, G., Klyatskaya, S., Auwärter, W., Neppl, S., Kern, K., Brune, H., Ruben, M. and Barth, J. V. Chiral kagome lattice from simple ditopic molecular bricks. *J. Am. Chem. Soc.* **130**, 11778 (2008).

Tomba, G., Colombi Ciacchi, L. and De Vita, A. Atomic-level studies of molecular self-assembly on metallic surfaces. *Adv. Mater.* **21**, 1 (2009).

Tseng, T.-C., Urban, C., Wang, Y, Otero, R., Tait, S. L., Alcamí, M., Écija, D., Trelka, M., Gallego, J. M., Lin, N., Konuma, M., Starke, U., Nefedov, A., Wöll, C., Ángeles Herranz, M., Martín, F., Martín, N., Kern, K. and Miranda, R. Charge transfer-induced structural rearrangements at both sides of organic/metal interfaces. *Nature Chem.* **2**, 374 (2010).

3.3 Self-Organised Hybrid Devices (SOHYD)

Principal Investigators

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Funding Organisations

Belgium: *Research Foundation Flanders*
Germany: *German Research Foundation*
Spain: *Interministerial Committee on Science and Technology*
Switzerland: *Swiss National Science Foundation*
United Kingdom: *Engineering and Physical Sciences Research Council*

The focus of the SOHYD project was the basic science relating to the function and development of self-organised nanomaterials for electronic devices. A key aim of the CRP was to bring organic and inorganic chemists, who have expertise in synthesising and developing new self-organising molecular structures based on chemical and biological motifs, together with physical chemists and physicists, who have expertise in developing and evaluating novel hetero-supermolecular functionalities and devices. This created a highly multidisciplinary collaboration with a combined skills set including inorganic, organic and polymeric semiconductor synthesis and processing, fundamental materials characterisation, device fabrication and testing, device physics and modelling, project management and technology transfer. Such appropriate combination of know-how made possible the synthesis and processing of semiconductors, material characterisation, device fabrication and testing as well as device physics and modelling. The main achievements of the CRP concern both basic and applied science and the quality of the research is of highest level. This is demonstrated by a number of research papers in high ranking journals and the knowledge transfer activities that have stemmed from the work. Both of these also prove an excellent level of integration between the groups of the CRP; the combination of expertise has resulted in several excellent scientific contributions.

Studies on charge separation and recombination in self-organising nanostructured donor–acceptor block copolymer films by the groups of Haque and Thelakkat show that donor–acceptor block copolymers can be used to control both the nanomorphology and the charge photogeneration. Specifically, this work focused on the development of quantitative structure–function relationships that can be used to rationally design self-organising molecular materials for photovoltaic device applications. It also demonstrated that the use of donor–acceptor block copolymers can be used to improve the performance of photovoltaic devices (compared to random blends). A key parameter controlling charge generation yield is the molecular weight of the block copolymer.

Collaboration between Torres-Cebada and Grätzel led to the ability to control nano-morphological organisation at the device level. The teams produced a new design for dye-sensitised solar cells in which high-energy photons are absorbed by highly photoluminescent chromophores unattached to the titania and undergoing Forster resonant energy transfer to the sensitising dye. This novel architecture allows for broader spectral absorption and an increase in dye loading, and relaxes the design requirements for the sensitising dye. A 26% increase in power conversion efficiency was demonstrated when using an energy relay dye with an organic sensitising dye.

Research was also carried out on light emitting diodes; work by the Haque group contributed to the fundamental understanding of light emitting diode function. They developed a hybrid inorganic–organic semiconductor light emitting diode based upon nanostructured hybrid metal oxide/polymer films, using ZrO_2 as an electron injection layer. These new devices offer the potential of both improved performance and lifetime and a US patent application has been filed on this invention.

Other notable results include:

- a new class of stable tetrathiafulvalene derivatives as metal-free organic dyes in dye-sensitised solar cells;
- use of copolymers of P3HT and side chain-functionalised thiophene derivatives for controlling nanomorphology in bulk heterojunction solar cells;
- improved understanding of the mechanisms of charge generation at quantum dot/metal oxide interfaces and the development of a new cobalt complex-based redox couple for use with quantum dot sensitisers, leading to CdSe quantum dot-sensitised solar cells exceeding efficiency 1% at full-sun intensity;
- slow electron injection on Ru-phthalocyanine sensitised TiO_2 – research which provided the basis

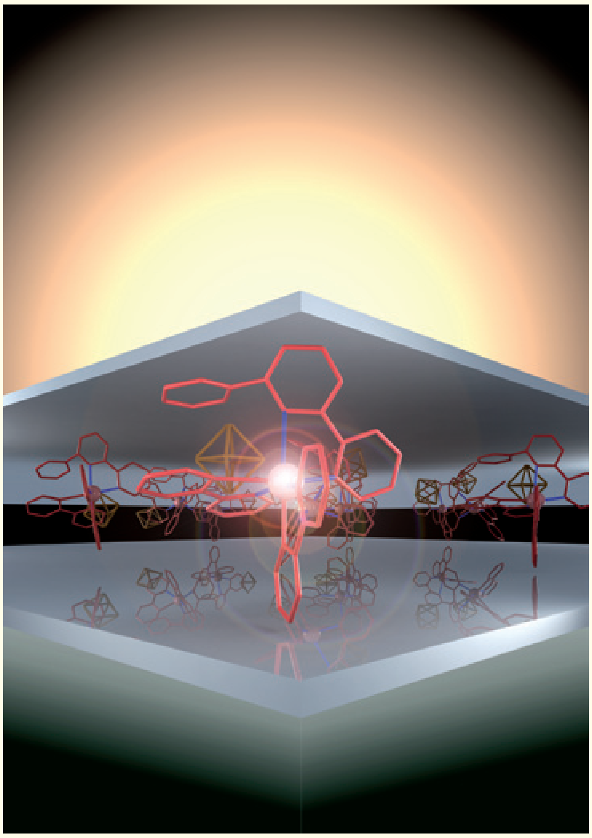

Figure 3.
By using an ionic iridium(III) complex containing supramolecularly-interacting ligands able to form a caged structure, the lifetime of light emitting electrochemical cells can be increased to more than 3000 hours paving the way for low-cost and large-area lighting and signing applications. *Adv. Mater.*, **20**, 3910 (2008). Reproduced with permission.

for new design rules for phthalocyanine sensitisers for dye-sensitised solar cells;

- the discovery that a key parameter controlling the dynamics of charge recombination in dye-sensitised metal oxide films is the spatial separation between the metal oxide surface and the dye cation moiety on the dye, facilitating the rational design and synthesis of molecular dyes for efficient dye-sensitised solar cells and a 25% improvement in device performance.

Two examples of technology transfer from the CRP involve three different principal investigators. Research headed by Coronado Miralles led to a significant increase in the lifetime of solid state light emitting electrochemical cells, from approximately 100 to more than 3000 hours. These results triggered the interest of OSRAM GmbH and with this company and other partners a FP7 project was submitted. The project, abbreviated as CELLO, was granted and launched in January 2010 (www.cello-project.eu). The other case, relates to the involvement of Vanderzande and Grätzel in the FP7 project, MOLESOL (http://www.molesol.eu/), in the area of third generation photovoltaic devices which was launched in October 2010. All the devices developed represent a potential alternative, low cost and high efficiency light source, contributing to the European Energy goals.

Selected publications

Bolink, H. J., Coronado, E., Costa, R. D., Ortí, E., Sessolo, M., Graber, S., Doyle, K., Neuburger, M., Housecroft, C. E. and Constable, E. C. Long-living light-emitting electrochemical cells – control through supramolecular interactions. *Adv. Mater.* **20**, 3910 (2008).

Fabregat-Santiago, F., Bisquert, J., Cevey, L., Chen, P., Wang, M., Zakeeruddin, S. M. and Grätzel, M. Electron transport and recombination in solid state dye solar cell with spiro-OMeTAD as hole conductor. *J. Am. Chem. Soc.* 131, 558 (2009).

Handa, S., Wietasch, H., Thelakkat, M., Durrant, J. R. and Haque, S. A. Reducing charge recombination losses in solid state dye sensitized solar cells: the use of donor–acceptor sensitizer dyes. *Chem. Commun.* **17**, 1725 (2007).

Hardin, B. E., Hoke, E. T., Armstrong, P. B., Yum, J.-H., Comte, P., Torres, T., Frechet, J. M. J., Nazeeruddin, Md. K., Graetzel, M. and McGehee, M. D. Increased light harvesting in dye-sensitized solar cells with energy relay dyes. *Nature Photon.* **3**, 406 (2009).

King, S., Sommer, M., Huetter, S., Thelakkat, M. and Haque. S. A. Charge separation and recombination in self-organizing nanostructured donor–acceptor block copolymer films. *J. Mater. Chem.* **19**, 5436 (2009).

Lee, H. J., Leventis, H. C., Moon, S.-J., Chen, P., Lto, S., Haque, S. A., Torres, T., Nüesch, F., Geiger, T., Zakeeruddin, S. M., Grätzel, M. and Nazeeruddin, Md. K. PbS and CdS quantum PbS and CdS quantum dot-sensitized solid-state solar cells: "old concepts, new results". *Adv. Funct. Mater.* **19**, 2735 (2009).

Lee, H. J., Yum, J. H., Leventis, H. C., Zakeeruddin, S. M., Haque, S. A., Chen, P., Seok, S. I., Graetzel, M. and Nazeeruddin, Md. K. CdSe quantum-dot sensitized solar cells exceeding 1% at full-sun intensity. *J. Phys. Chem. C* **112**, 11600 (2008).

Li, T. C., Goes, M. G., Fabregat-Santiago, F., Bisquert, J., Bueno, P. R., Prasittichai, C., Hupp, J. T. and J. T. and Marks, T. J. Surface passivation of nanoporous TiO_2 via atomic layer deposition of ZrO_2 for solid-state dye-sensitized solar cell applications. J. Phys. Chem. C 113, 18385 (2009).

Moehl, T., Kytin, V. G., Bisquert, J., Kunst, M., Bolink, H. J. and Garcia-Belmonte, G. Relaxation of photogenerated carriers in P3HT:PCBM organic blends. *ChemSusChem* **2**, 314 (2009).

Wenger, S., Bouit, P. A., Chen, Q., Teuscher, J., Di Censo, D., Humphry-Baker, R., Moser, J. E., Delgado, J. L., Martín, N., Zakeeruddin, S. M. and Grätzel M. Efficient electron transfer and sensitizer regeneration in stable π-extended tetrathiafulvalene-sensitized solar cells. *J. Am. Chem. Soc.* **132**, 5164 (2010).

3.4 **Crystals Nano-particles (LC-NANOP)**

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Funding Organisations

Germany: *German Research Foundation*
Poland: *Polish Academy of Sciences*
United Kingdom: *Engineering and Physical Sciences Research Council*

LC-NANOP aimed to develop a new approach to the self-organisation and self-assembly of organic, inorganic and metal nanoparticles (NPs) using the unique self-organisation properties of liquid crystals (LCs) to propagate order over large length scales. Thus LC-NANOP was concerned with the synthesis, characterisation and properties of super- and supramolecular systems which are formed by deploying a NP as a central scaffold and surrounding it with a coat of LC. The methodologies ranged from synthesis to sophisticated analytical tools, to application-oriented characterisation of the electric, magnetic, optoelectronic and photonic properties, and the simulation of the mesophases obtained. One new technique developed in the project was a preparation method that allows microscopic imaging of LC director fields in complex geometries, and in particular in the vicinity of micro- and NPs by means of fluorescence confocal polarising microscopy.

The CRP facilitated interaction between individual projects which were specialised in different fields of synthetic chemistry, analytical and physical chemistry, physics and chemical engineering, providing an excellent platform for the development of multidisciplinary research. The direct feedback between the synthesis, the characteristics of the materials applications, their performance and their simulation was found to be particularly beneficial.

By developing new self-assembling approaches the CRP gave rise to organic, inorganic and metal-based NPs. In particular, NP central scaffolds have been surrounded with coats of LCs, in order to obtain super- and supramolecular systems. A number of interesting nanoassemblies with potential applications in different research fields but which also provide key information on some basic research have been achieved. These include self-organising Au, Co, Pt, metal oxide and ferromagnetic NPs grafted with a soft, adaptive organic layer made of LC thiol molecules. Depending on the molecular structure of the thiols lamellar, columnar or cubic phases were observed. The structures, seemingly non-compatible with the spherical shape of NPs, were obtained because of the self-segregation of mesogenic and simple n-alkyl ligands at the NP surfaces. Supermolecular systems were created based on a central scaffold with mesogenic groups attached to the scaffold to provide self-organisation, and in addition a functional unit was also incorporated into the structure. The mesogenic groups included cyanobiphenyls, whereas the functional groups included fullerenes, fluorenes, perylenes, porphyrins, etc (i.e. fluorescent and semi-conducting units).

Two novel systems produced by the CRP particularly stand out: the first examples of Janus dendritic LCs were created where one face of the supermolecules was composed of disc-like LCs, whereas the other face was composed of rod-like liquid crystals. These systems microphase segregated. Additionally, the first examples of complex mesogenic structures formed by bent-core mesogens attached to dendrimeric dendritic scaffolds were created. These were predicted to exhibit unusual ferroelectric behaviour.

Both self-organising metamaterials and ferromagnetic systems were prepared: LC-coated gold NPs were found to self-organise and to exhibit surface plasmon effects that were wavelength dependent with respect to the nature of the LC coating. Mesomorphic dendronised NPs exhibited room

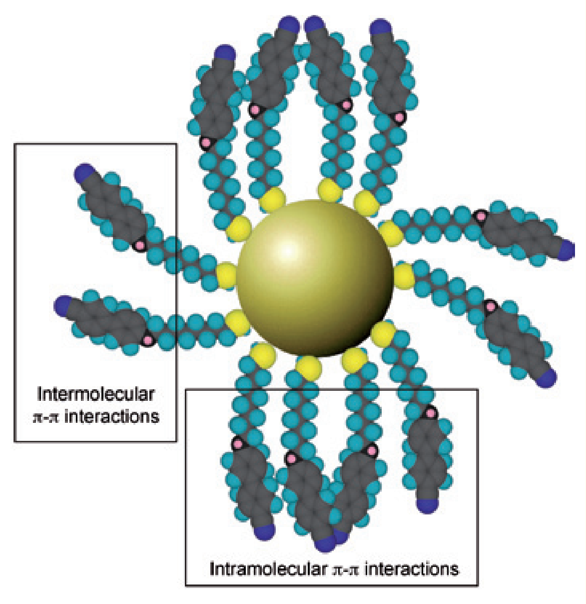

Figure 4.
Topological distortion caused by inter- and intramolecular interactions for a gold nanoparticle coated with *ω-8*-(4-cyanobiphenyl-4’-yloxy)alkanethiols. Draper, M., Saez, I. M., Cowling, S. J., Gai, P., Heinrich, B., Donnio, B., Guillon D. and Goodby, J. W. Self-Assembly and Shape Morphology of Liquid Crystalline Gold Metamaterials. *Adv. Funct. Mater.*, **21**, 1260 (2011). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

temperature ferromagnetism and Mn clusters prepared. In addition, magnetic (Co) and non-magnetic (Pt) NPs were functionalised by variety of mesogenic molecules.

Some of the assemblies created displayed interesting optical effects. Chiral NPs based on sugar scaffolds with LC coatings were prepared and the transmission of the chirality from the interior to the exterior of the particles was investigated. These NPs were found to induce iridescence in nematic LCs. Investigations of the photorefractive effect in polymer-dispersed LCs indicate that the efficiency of the photorefractive effect (optical gain) can be enhanced by doping of the polymer matrix. Although small molecules were used as dopants, similar effects can be expected to appear by doping with NPs. One system exhibited modified anchoring and thus a complete reversal of the electro-optic switching from bright (field-off)/dark (field-on) to dark (field-off)/bright (field-on). A detailed study of this system gave evidence that the behaviour is due to non-standard electroconvection. Tuneable light sources have been have been fabricated by embedding semiconductor microresonators that contain luminescent quantum dots in LCs. In these systems, controlled shifts of the resonance frequency of whispering gallery modes have been demonstrated.

Many of the results were found to be applicable to other research areas including (opto)electronic devices. Three examples are, the synthesis of liquid-crystalline dendrimers that improved the morphology of semiconducting composites for organic photovoltaics and semi-conductors; a demonstration of the benefit of ordering monodisperse liquid crystal oligomers for linearly polarised emission of light from OLEDs and, in collaboration with a SUPRAMATES project, the development of novel transparent graphene electrodes for LC addressing which could be used to replace indium-tin-oxide.

Selected publications

Campidelli, S., Bourgun, P., Guintchin, B., Furrer, J., Stoeckli-Evans, H., Saez, I. M., Goodby, J. W. and Deschenaux, R. Diastereoisomerically pure fulleropyrrolidines as chiral platforms for the design of optically active liquid crystals. *J. Am. Chem. Soc.* **132**, 3574 (2010).

Kasdorf, O., Kitzerow, H.-S., Lenoble-Zwahlen, J. and Deschenaux, R. Influence of a mesogenic dendrimer on the morphology of polymer-fullerene composites for photovoltaics. *Jpn. J. Appl. Phys.* **49**, 01AF01 (2010).

Lincker, F., Bourgun, P., Stoeckli-Evans, H., Saez, I. M., Goodby J. W. and Deschenaux, R. Optically active liquid-crystalline fullerodendrimers from enantiomerically pure fulleropyrrolidines. *Chem. Commun.* **46**, 7522 (2010).

Maringa, N., Lenoble, J. L., Donnio, B. Guillon, D. and Deschenaux, R. Liquid-crystalline methanofullerodendrimers which display columnar mesomorphism. *J. Mater. Chem.* **18**, 1524 (2008).

Nordendorf, G., Kasdorf, O., Kitzerow, H.-S., Liang, Y., Feng, X. and Müllen, K. Liquid crystal addressing by graphene electrodes made from graphene oxide. *Jpn. J. Appl. Phys.* **49**, 100206 (2010).

Piegdon, K. A., Declair, S., Förstner, J., Meier, T., Matthias, H., Urbanski, M., Kitzerow, H.-S., Reuter, D., Wieck, A. D., Lorke, A. and Meier, C. Tuning quantum-dot based photonic devices with liquid crystals. *Opt. Express* **18**, 7946 (2010).

Redler, A. and Kitzerow, H.-S. Influence of doping on the photorefractive properties of a polymer-dispersed liquid crystal. *Appl. Phys. Lett.* **93**, 183304 (2008).

Urbanski, M., Kinkead, B., Qi, H., Hegmann, T. and Kitzerow, H.-S. Electroconvection in nematic liquid crystals via nanoparticle

doping, *Nanoscale* **2**, 1118 (2010).
Wojcik, M., Mieczkowski, J.,, Pociecha, D. and Gorecka, E. Multidimensional structures made by gold nanoparticles with shape-adaptive grafting layer. *Soft Matter* **6**, 5397 (2010).
Wolska, J., Mieczkowski, J., Pociecha, D., Buathong, B., Donnio, B., Guillon, D. and Gorecka, E. Mesomorphism of protodendritic oligomers. *Macromolecules* **42**, 6375 (2009).

3.5 Complexity Across Lengthscales in Soft Matter (SCALES)

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Associated Partner

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Funding Organisations

Germany: *German Research Foundation*
Poland: *Polish Academy of Sciences*
United Kingdom: *Engineering and Physical Sciences Research Council*

The objective of the SCALES CRP was to combine the expertise of groups involved in complementary aspects of research into soft matter with complex self-organisation on different length scales. In particular the project focused on novel highly complex structures formed by liquid crystals (LCs) and star block copolymers consisting of three and four incompatible types of moiety.

The international cooperation facilitated by the EUROCORES programme enabled access to specialist knowledge and research facilities not available in each individual country – no one country could have afforded a match of the quality and diversity of the combined expertise. Interdisciplinarity was the cornerstone of this project and gathering together synthetic and physical chemists from the fields of low molecular weight compounds and polymers, as well as physicists, structural, material and simulation scientists proved highly successful and productive.

The CRP made significant contributions to the understanding of fundamentals of building hierarchical order in nanostructured LC systems, and brought structural variety and complexity in soft matter to a qualitatively new level. The combination of organic synthesis with sophisticated X-ray scattering, NMR and high-resolution AFM methods, colloid and surface science and computer simulation worked extremely well in achieving the multitude of fundamentally new findings. New areas in organised soft matter were opened up: multicolour tiling and low-symmetry three-dimensional (3D) mesostructures; and it showed how large periodicities and novel symmetries can be generated with small molecules based on colour and volume frustration. Furthermore, significant progress was made towards low-molar LC–block copolymer hybrids by establishing general principles for the design of space-partitioned mesostructures with two-dimensional (2D) and 3D periodicity – focusing on molecules with star-branched topology – bridging a traditional length-scale divide.

The first examples of multicolour tiling patterns in liquid crystals were honeycomb nanostructures with cells of between two and five different compositions (“colours”) and polygonal shapes. “Honeycomb-in-honeycomb” hybrid structures with amphiphile LC infiltrated nanoporous alumina gave rise to the effect of nano-confinement which was determined using 3D-XRD and NMR. Further honeycomb and other LC phases discovered and characterised include giant 10-hexagonal cylinder arrays, triangular, trapezoidal, mixed octagonal and other cylinder arrays, the first example of a columnar phase with non-centrosymmetric trigonal symmetry, and a number of unusual and extremely complex 2D structures. The new types of 3D-ordered LC phases have symmetries ranging from cubic to triclinic in T- and X-shaped amphiphiles.

The project also introduced a new type of order–disorder transitions and critical phenomena in soft matter; these occur between multicolour and monochrome tilings in liquid crystals and are analogous to ferro- and antiferromagnets.

Work carried out in the CRP created interesting potential avenues towards new photonic and nonlinear optical materials, including the design and experimental verification of first “axial calamitic bundle” columnar phases and of their segmentation into 3D ordered structures, with important implications for design of oriented OLEDs, organic transistors, and photovoltaic devices; the establishment of new ways of creating nanoparticle strings with controlled interparticle spacing, hence plasmonic resonance, using coating with LC ligands; and significant progress towards new types of soft quasicrystals.

Other notable achievements include:

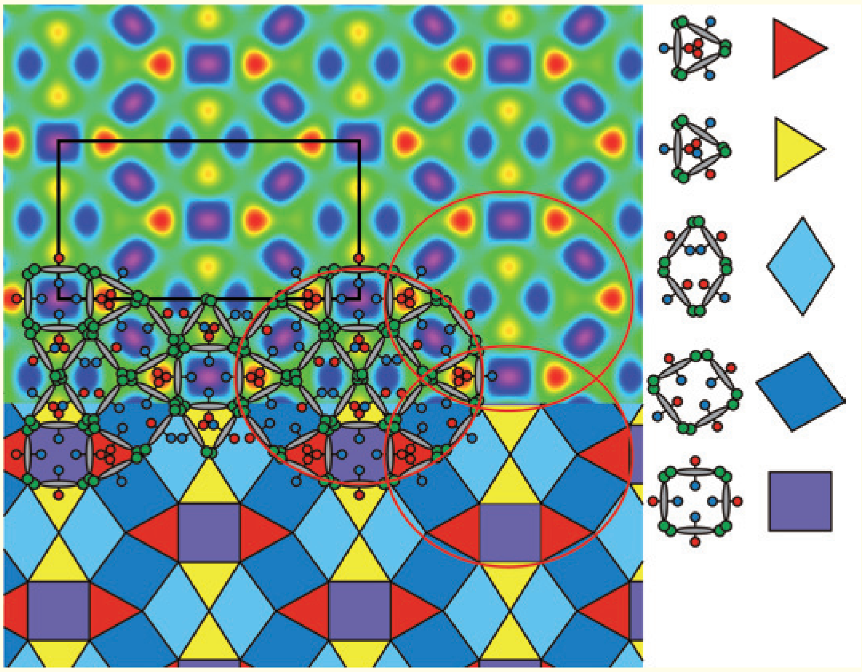

Figure 5.
Complex tiling patterns in liquid crystal honeycombs of a tetraphilic X-shaped compound with a oligo(phenyleneethinylene)-based rigid rod core. Top, electron density maps of the *p2mm* and *c2mm* phases, with schematic molecules overlaid (gray rods denote aromatic cores, green dots the glycerol groups, and red and blue dots the Si and F chains); black rectangle is the unit cell. Bottom, tiling patterns corresponding to the electron density maps. Side, the three and five types of tiles which, through tessellation, form the *p2mm* and *c2mm* honeycombs. From Zeng, X. B. *et al. Science*, **331**, 1302 (2011). Reprinted with permission from AAAS.

- discovery of six-stranded hollow helical self-assembly in a LC heterohelicene – the most detailed structure determination of an "ordered columnar" phase so far, with implications for enantiospecific molecular sieves;
- significant advances in understanding the helical superstructure in linear triblock terpolymers and in controlling their alignment;
- self-assembly of 3-miktoarm star terpolymer on preconditioned substrates with the aim to perpendicularly align the cylindrical microdomain on a porous substrate;
- discovery of new amphiphiles forming well-defined and stable Langmuir mono- and multi-layers with hysteresis-free pressure-area isotherms; moreover, these compounds allow, for the first time, the preparation of well-defined multilayer Langmuir-Blodgett films in a single dipping run;
- discovery of 3D correlated structures in helical achiral block copolymers.

As well as constructing new materials, research in the project increased the sophistication of structural characterisation and computer simulation methods. More specifically, significant improvements in methods of soft mesostructure determination included development of GISAXS for complex LCs, construction of 3D diffraction pattern, introduction of the high-sensitivity torsional resonance AFM, isomorphous replacement in combined small-angle X-ray and neutron diffraction and enhanced methods for solving the phase problem in mesocale crystallography. Theoretical work developed dissipative particle dynamics with demonstrated ability to predict new phase structures.

Selected publications

Bates, M. A. and Walker, M. Dissipative particle dynamics simulation of T- and X-shaped polyphilic molecules exhibiting honeycomb columnar phases. *Soft Matter* **5**, 346 (2009).

Glettner, B., Liu, F., Zeng, X. B., Prehm, M., Baumeister, U., Bates, M. A., Walker, M., Boesecke, P., Ungar, G. and Tschierske, C. Liquid crystalline kagome. *Angew. Chem. Int. Ed.* **47**, 9063 (2008).

Glettner, B., Liu, F., Zeng, X. B., Prehm, M., Baumeister, U., Ungar, G. and Tschierske, C. Liquid crystal engineering with anchor-shaped molecules: Honeycombs with hexagonal and trigonal symmetries formed by polyphilic bent-core molecules. *Angew. Chem. Int. Ed.* **47**, 6080 (2008).

Jinnai, H., Kaneko, T., Matsunaga, K., Abetz, C. and Abetz, V. A double helical structure formed from an amorphous, achiral ABC triblock terpolymer. *Soft Matter* **5**, 2042 (2009).

Niton, P., Żywociski, A., Hołyst, R., Kieffer, R., Tschierske, C., Paczesny, J., Pociecha, D. and Gorecka, E. Reversible aggregation of X-shaped bolaamphiphiles with partially fluorinated lateral chains at the air/water interface. *Chem. Commun.* **11**, 1896 (2010).

Prehm, M., Liu, F., Baumeister, U., Zeng, X. B., Ungar, G. and Tschierske, C. The gianthexagon cylinder network-a liquid crystalline organization formed by t-shaped quaternary amphiphiles. *Angew. Chem. Int. Ed.* **46**, 7972 (2007).

Prehm, M., Liu, F., Zeng, X., Ungar, G. and Tschierske, C. Axial-bundle phases--new modes of 2D, 3D, and helical columnar self-assembly in liquid crystalline phases of bolaamphiphiles with swallow tail lateral chains. *J. Am. Chem. Soc.* **133**, 4906 (2011).

Szymborski, T., Cybulski, O., Bownik, I., Żywociski, A., Wieczorek, S. A., Fiałkowski, M., Hołyst, R. and Garstecki, P. Dynamic charge separation in a liquid crystalline meniscus. Soft Matter **12**, 2352 (2009).

Zeng, X. B., Kieffer, R., Glettner, B., Liu, F., Pelz, K., Prehm, M., Baumeister, U., Hahn, H., Lang, H., Gehring, G. A., Weber, C. H. M., Hobbs, J. K., Tschierske, C. and Ungar, G. Complex multicolor tilings and critical phenomena in tetraphilic liquid crystals. *Science* **331**, 1302 (2011).

3.6 Biofunctional Self-Organised Nano-Structures of Ionic/Non-ionic Amphiphilic Copolymers, Biopolymers-Biomacromolecules and Nanoparticles: From Bioinspired to Biointegrated Systems (BIOSONS)

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Funding Organisations

Czech Republic: *Czech Science Foundation*
Germany: *German Research Foundation*
Switzerland: *Swiss National Science Foundation*

BIOSONS focused on developing a new generation of bio-inspired and biologically modified self-assembling materials and SONS. Biology offers a window to the most sophisticated collection of functional nanostructures that exists, and starting from the well-established rationale for self-assembling block copolymers, the CRP aimed to introduce the resources that can be found in biological systems.

The research carried out is multidisciplinary and the success of the CRP was achieved thanks to a strongly complementary consortium – it contained groups with biological, chemical and physical expertise. Furthermore, both theoreticians and experimentalists worked in close collaboration. The specialists in modelling and predicting tools established the theoretical framework at the initial, intermediate and final stages of the task development. Within this framework, material developers provided all the materials, while those groups having expertise in advanced experimental characterisation studied the numerous SONS created, as well as their behaviour under different external fields and stimuli.

The approach was split into three stages in which the role of synthetic polymers was progressively substituted by sophisticated biological molecules. First, biological functions (by selected peptides and oligonucleotides) were coupled to self-assembling synthetic polymers as a way to boost their (bio)functionality. After this, self-assembling and selective-binding parts taken from natural proteins and oligonucleotides were combined with synthetic polymers to improve their ability to self-assemble and show specific interactions. Finally, in the last stage, biological complex materials, which have clear potential to enhance the capacity for both self-assembly and (bio)function were exclusively employed.

This resulted in the preparation of new, bio-inspired and biological materials that interface synthetic and living matter as well as developing a better understanding of the processes occurring at these interfaces. For example, an investigation into the mineralisation of calcium phosphate in the presence of engineered proteins and at the interface of charged block copolymer monolayers at the air–water interface showed that controlled interactions of the growing nuclei with the (bio) polymer interface control the mineralisation process at different hierarchical levels ranging from the atomic level (crystal structure) to the macroscopic scale (defined packing of nanoparticles into a superlattice). Another example is the use of block copolymer membranes with inserted Aquaporin Z

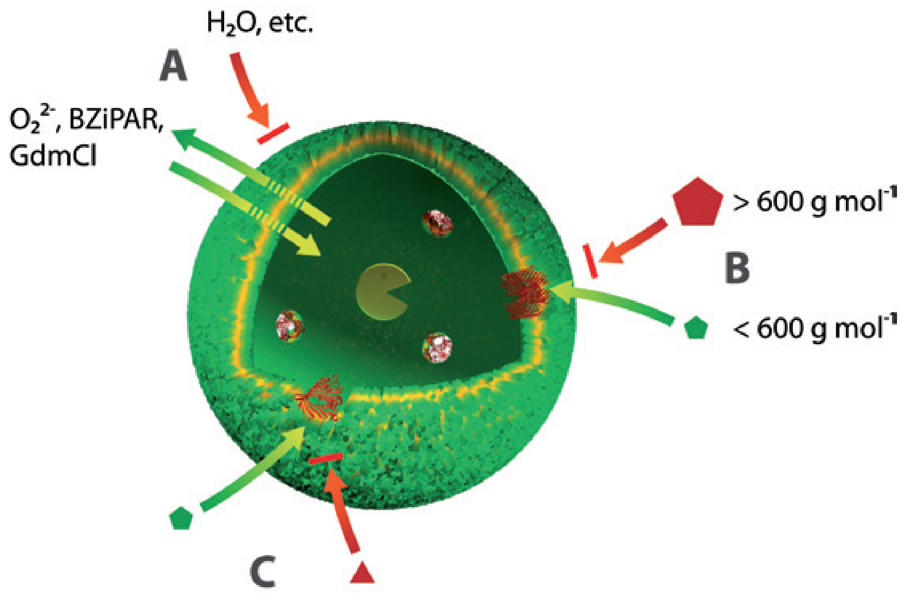

Figure 6.
Illustration of selective access to PMOXA-*b*-PDMS-*b*-PMOXA polymersomes. **A,** The membrane itself shows permeability to a small number of molecules only. **B, C,** Selective access into and egress out of the inner cavity can be achieved by reconstitution of membrane proteins in the block copolymer membrane. Renggli, K., Baumann, P., Langowska, K., Onaca, O., Bruns, N. and Meier, W. Selective and Responsive Nanoreactors. *Adv. Funct. Mater.* **21**, 1241 (2011). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

as a new approach for developing highly permeable membranes for water filtration. Here a naturally occurring functional unit was successfully integrated into a synthetic polymer membrane and allows water filtration with an unprecedented selectivity and efficiency.

One particular highlight is the fabrication of new, nanostructured surfaces that are able to actively produce bioactive compounds. These are of great interest because of their potential use as tools for applications in synthetic biology, biochemical engineering and materials science, for instance as new antibacterial implant surfaces or as biosensors with enhanced sensitivity. Other results with potential for practical applications include the development of tools for selective immobilisation of nanoreactors for investigation of enzymatic reactions down to a single molecule level and the local production of bioactives. The reactions carried out so far already demonstrate the future potential application of the system in sensors, analytics, microfluidics, and single-molecule spectroscopy.

Progress in the field generated by BIOSONS is also demonstrated by the following outcomes:

- development of a modular synthetic route to well-defined bio-functional/responsive homopolymers and copolymers, based on metal-free ring-opening polymerisation and thiol-ene "click" photochemistry;
- self-assembly of bioorganic–synthetic hybrid (co-)polymers in dilute aqueous solution;
- hierarchical structure formation of polypeptide–poly(ethylene oxide) block copolymers and blends in thin film solution;
- development of a better understanding of the interaction of proteins with charged surfaces;
- the first experimental evidence of controlled self-assembly of a purely hydrophilic block copolymer in water.

Overall, significant steps forward were made in terms of creating new biofunctional self-assembled nanostructures based on amphiphilic polymers, peptides and proteins. The results of the physico-chemical experiments gave new insight into the interactions between biological and synthetic molecules, and allowed the development of new tools for investigating the behaviour of individual biological molecules or the effect of spatial confinement and local crowding on biological reaction pathways.

Selected publications

Ben-Haim, N., Broz, P., Marsch, S., Meier, W. and Hunziker, P. Cell-specific integration of artificial organelles based on functionalized polymer vesicles. *Nano Lett.* **8**, 1368 (2008).

Botiz, I., Schlaad, H. and Reiter, G. Processes of ordered structure formation in polypeptide thin film solutions. *Adv. Polym. Sci.* **239**, 1 (2011).

Casse, O., Colombani, O., Kita-Tokarczyk, K., Müller, A. H. E., Meier, W. and Taubert, A. Calcium phosphate mineralization beneath monolayers of poly(n-butylacrylate)–block–poly(acrylic acid) block copolymers. *Faraday Discuss.* **139**, 179 (2008).

Gromadzki, D., Lokaj, J., Černoch, P.,

Diat, O., Nallet, F. and Štěpánek, P. Morphology of polystyrene-block-poly(styrene-co-acrylonitrile) and polystyrene-block-poly(styrene-coacrylonitrile-co-5-vinyltetrazole) diblock copolymers prepared by nitroxidemediated radical polymerization and "click" chemistry. *Eur. Polym. J.* **44**, 189 (2008).

Grzelakowski, M., Onaca, O., Rigler, P., Kumar, M. and Meier, W. Immobilized protein–polymer nanoreactors. *Small* **5**, 2545 (2009).

Henzler, K., Haupt, B., Lauterbach, K., Wittemann, A., Borisov, O. and Ballauff, M. Adsorption of beta lactoglobulin on spherical polyelectrolyte brushes: direct proof of counterion release by isothermal titration calorimetry. *J. Am. Chem. Soc.* **132**, 3159 (2010).

Koňák, Č., Šubr, V., Kostka, L., Štěpánek, P., Ulbrich, K. and Schlaad, H. Coating of vesicles with hydrophilic reactive polymers. *Langmuir* **24**, 7092 (2008).

Kumar, M., Grzelakowski, M., Zilles, J., Clark, M. and Meier, W. Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z. *Proc. Natl. Acad. Sci. USA* **104**, 20723 (2007).

Polotsky, A. V., Charlaganov, M. I., Xu, Y., Leermakers, F. A. M., Daoud, M., Müller, A. H. E. and Borisov, O. V. Pearl-necklace structures in core-shell molecular brushes: experiments, monte carlo simulations and self-consistent field modelling. *Macromolecules* **41**, 4020 (2008).

Walther, A., Drechsler, M., Rosenfeldt, S., Harnau, L., Ballauff, M., Abetz, V. and Müller, A. H. E. Self-assembly of Janus cylinders into hierarchical superstructures. *J. Am. Chem. Soc.* **131**, 4720 (2009).

3.7 Self-Assembled Nanoscale Magnetic Networks (SANMAG)

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Funding Organisations

Austria: *Austrian Science Fund*
Germany: *German Research Foundation*
Italy: *National Research Council*
Switzerland: *Swiss National Science Foundation*

Elemental and alloyed nanomagnets of controlled size organised into regular patterns offer new perspectives for exciting developments in the timely fields of nanoelectronics, spintronics, and quantum computation. The intention of the SANMAG CRP was to exploit self-assembly processes for creating and developing bottom-up architectures of planar magnetic networks constituted by sub-nanometre-size functional elements. More specifically, it aimed to develop self-assembly strategies to design nanomagnetic networks by controlling the specific properties of individual atomic-scale magnets, their mutual interactions, and coupling with the environment. By combining theoretical, microscopy, magnetometry, and spectroscopy methods in order to obtain an in-depth understanding of the synthesis, structural, electronic and magnetic properties of novel nanoscale magnetic systems, the project gave rise to several innovative scientific insights on fundamental and functional properties of self-assembled magnetic networks. New self-assembly strategies were devised in order to design fine-structured magnetic architectures and tune their magnetic behaviours. Accurate control on the atomic scale led to significant progress in the description of individual sub-nanometre magnetic particles, the mutual interactions among magnetic units, and their coupling with the environment.

Very interesting novel magnetic structures were fabricated by exploiting self-organisation processes following metal beam deposition on nanopatterned templates. Extremely high areal density superlattices of magnetic Co islands, decorated with Fe at their borders, produced on vicinal metal surfaces were examined. Uniform island patterns were obtained with a period of 72 Å x 58 Å, equivalent to a density

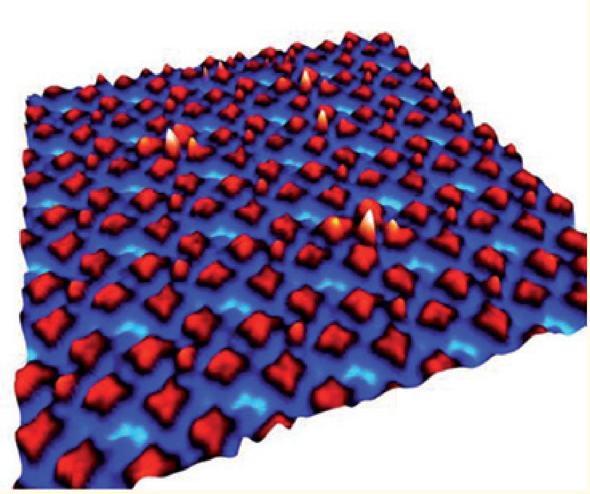


Figure 7.
Scanning tunnelling microscope image of the two-dimensional metal–organic iron network self-assembled on copper. From : Gambardella, P. *et al.* Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface *Nature Mater.* **8**,189 (2009).

(15 Tera units in^{-2}) two orders of magnitude larger than the previous generation of commercial hard-disks. Their uniaxial out-of-plane magnetisation, negligible mutual magnetic interactions, and narrow distributions of magnetic anisotropies, moments and switching fields make these superlattices ideal models for exploring the ultimate density limits of magnetic recording. Effective tuning of their functional properties was achieved by accurate control of the chemical composition of the magnetic particles. The high blocking temperatures of pure Co islands, which reverse their magnetisation by coherent rotation, could be significantly enhanced by decorating their perimeter with Fe. In particular, blocking temperatures as high as 105 K were obtained for small Fe-decorated Co islands with a mean size of only 490 atoms.

New magnetic phenomena were discovered, such as spin spirals which were found in nanostructures, and shown to be caused by the Dzyaloshinskii–Moriya interaction. As well as this, directional and focussing effects caused by the Ruderman–Kittel–Kasuya–Yosida interaction were revealed.

The collaborative research among the partners has been very extensive at all stages of the programme development and the successes have been largely based on the efficient share of the groups' competences. The partners from Stuttgart, Lausanne, Trieste, Vienna, and Barcelona collaborated in several joint projects on metallic and molecular magnetic networks, making extensive use of complementary methods, such as scanning tunnelling microscopy for structural characterisations and synchrotron-based techniques for spectroscopic and magnetometric investigations. The Jülich group provided theoretical support for defining the objective of the investigations and contributed to the analysis of the results obtained by the experimental groups. The strong degree of interaction among the partners is demonstrated by the number and high level of the joint publications. Among the prominent collaborative results which have been obtained in the frame of the project are those of the Jülich and Trieste groups on monatomic metal wires, and achieving the controlled modification of the magnetic anisotropy in two-dimensional molecular arrays by the Barcelona–Lausanne–Stuttgart groups through their work on two-dimensional supramolecular magnetic structures. Furthermore, research carried out in Trieste and Barcelona produced an analysis of correlation effects in three dimensional magnetic atoms on surfaces, and a collaboration between Stuttgart and Vienna on two-dimensional magnetic alloys resulted in the observation of complex magnetic 2D-alloy phases.

The activity developed in the frame of the CRP has fully demonstrated the feasibility of tuning and controlling magnetic properties of miniaturised functional magnetic elements in atomic-scale structures, built by self-assembly processes. A remarkable degree of flexibility in engineering functional properties has been shown to be achievable through a high precision design of multi-elements structures, such as supramolecular assemblies and nanoscale metal clusters on surfaces.

Selected publications

Błoński, P., Lehnert, A., Dennler, S., Rusponi, S., Etzkorn, M., Moulas, G., Bencok, P., Gambardella, P., Brune, H. and Hafner, J. Magnetocrystalline anisotropy energy of Co and Fe adatoms on the (111) surfaces of Pd and Rh. *Phys. Rev. B* **81**, 104426 (2010).

Carbone, C., Veronese, M., Moras, P., Gardonio, S., Grazioli, C., Zhou, P. H., Rader, O., Varykhalov, A., Krull, C., Balashov, T., Mugarza, A., Gambardella, P., Lebeque, S., Eriksson, O., Katsnelson, M. I. and Lichtenstein, A. I. Correlated electrons step by step: itinerant-to-localized transition of Fe impurities in free-electron metal hosts. *Phys. Rev. Lett.* **104**, 117601 (2010).

Ferriani, P., von Bergmann, K., Vedmedenko, E.Y., Heinze, S., Bode, M., Heide, M., Bihlmayer, G., Blügel, S. and Wiesendanger, R. Atomic-scale spin spiral with a unique rotational sense:

Mn monolayer on W(001), *Phys. Rev. Lett.* **101**, 027201 (2008).

Gambardella, P., Stepanow, S., Dmitriev, A., Honolka, J., de Groot, F. M. F., Lingenfelder, M., Gupta, S. S., Sarma, D. D., Bencok, P., Stanescu, S., Clair, S., Pons, S., Lin, N., Seitsonen, A. P., Brune, H., Barth, J. V. and Kern, K. Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface. *Nature Mater.* **8**, 189 (2009).

Honolka, J., Lee, T.-Y., Kuhnke, K., Enders, A., Skomski, R., Bornemann, S., Mankovsky, S., Minar, J., Staunton, J., Ebert, H., Hessler, M., Fauth, K., Schütz, G., Buchsbaum, A., Schmid, M., Varga, P. and Kern, K. Magnetism of FePt surface alloys. *Phys. Rev. Lett.* **102**, 067207 (2009).

Honolka, J., Lee, T.-Y., Kuhnke, K., Repetto, D., Sessi, V., Wahl, P., Buchsbaum, A., Varga, P., Gardonio, S., Carbone, C., Krishnakumar, S. R., Gambardella, P., Komelj, M., Singer, R., Fähnle, M., Fauth, K., Schütz, G., Enders, A. and Kern, K. Complex magnetic phase in submonolayer Fe stripes on Pt(997). *Phys. Rev. B* **79**, 104430 (2009).

Stepanow, S., Mugarza, A., Ceballos, G., Moras, P., Cezar, J. C., Carbone, C. and Gambardella, P. Giant spin and orbital moment anisotropies of a Cu-phthalocyanine monolayer. *Phys. Rev. B* **82**, 014405 (2010).

Weismann, A., Wenderoth, M., Lounis, S., Zahn, P., Quaas, N., Ulbrich, R. G., Dederichs, P. H. and Blügel, S. Seeing the Fermi-surface in real space by nanoscale electron focusing. *Science* **323**, 5918 (2009).

Zhou, P. H., Moras, P., Ferrari, L., Bihlmayer, G., Blügel, S. and Carbone, C. One-dimensional 3d electronic bands of monoatomic Cu chains. *Phys. Rev. Lett.* **101**, 036807 (2008).

Zhou, L., Wiebe, J., Lounis, S., Vedmedenko, E., Meier, F., Blügel, S., Dederichsm P. H. and Wiesendanger, R. Strength and directionality of surface Ruderman–Kittel–Kasuya–Yosida interaction mapped on the atomic scale. *Nature Phys.* **6**, 187 (2010).

4.

Networking and Dissemination Activities

Networking and dissemination activities are key characteristics of a EUROCORES programme such as SONS II. Their aim is to encourage and facilitate scientific collaboration and diffusion across the CRPs within a given domain or, if appropriate, across different domains and programmes. These activities are flexible and can be tailored to the needs of a given programme.

Networking activities are collaborative activities bringing together scientists from EUROCORES programmes and colleagues from other relevant programmes in order to discuss, plan and implement future collaboration and interaction. Typical examples are:

- working group meetings, seminars, workshops, symposia, conferences;
- summer schools (targeted to members of academia, the private sector and governmental or non-governmental organisations);
- training programmes and specialised courses (graduate-level and continuing-education);
- short visits.

Dissemination activities are all the activities that are carried out with the aim of raising awareness and diffusing results of the EUROCORES programme. These include:

- leaflets, posters, publications, books, exhibition booth or stand at a conference;
- invited sessions at larger conferences (when the EUROCORES programme is not directly involved in the conference as a main or co-organiser of the event);
- dissemination travel grants, to support active participation at conferences (organised outside the EUROCORES programme), while promoting the EUROCORES scheme in general and disseminating the achievements of the programme in particular.

For SONS II the principal networking activities were a series of conferences, workshops and international schools as well as short visits and exchanges. Among the dissemination activities were presentations by the PIs as invited speakers at conferences,

Figure 8.
Participants of the Symposium on Self-Organised Nanostructures in Liquid Crystals

and press releases. Many joint publications appeared in peer-reviewed journals and two notable highlights are the special issues of *Advanced Materials* and *Advanced Functional Materials*.

The research results presented at the E-MRS SONS II symposium in May 2008 were featured in an issue of *Advanced Materials*, From Supramolecules to Suprafunctions. The issue features an editorial (Paolo Samorì, Franco Caccialli, Giovanni Marletta, Roberto Faria and Mario Ruben), an essay on the ESF involvement in materials science research (Antonella di Trapani) and a series of articles by SUPRAMATES and FunSMARTs II researchers. *Adv. Mater.* **21**(10–11) 2009.

Paolo Samorì and Franco Cacialli (SUPRAMATES), Fabio Biscarini (FunSmart II) and Ana Helman (ESF) were guest editors of a special issue on "Multiscale Self-Organization of Functional Nanostructures" of the journal *Advanced Functional Materials* (**21**(7) 2011). The issue highlights work from SONS II and contains six feature articles summarising the achievements of SONS II CRPs.

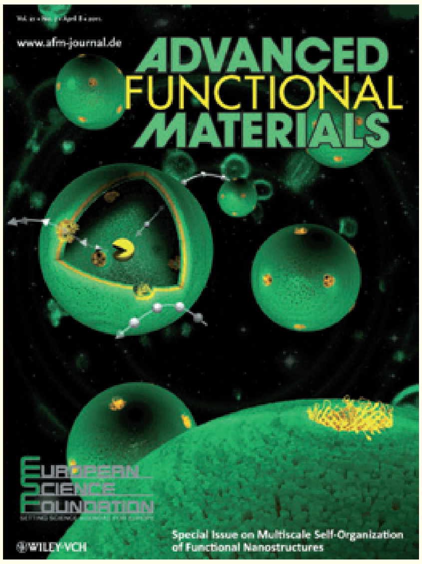
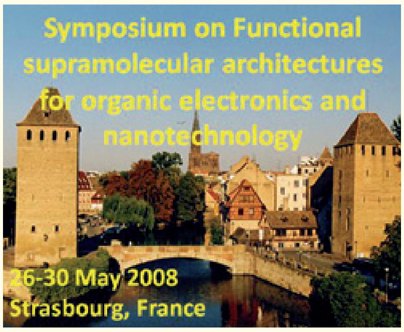


Figure 9.
Renggli, K., Baumann, P., Langowska, K., Onaca, O., Bruns, N. and Meier, W. Nanoreactors: Selective and Responsive Nanoreactors. Cover of *Advanced Functional Materials*, Vol 21, Issue 7, Copyright 2011, Wiley-VCH.



- **European Materials Research Society (E-MRS) SONS II Symposium**
  Strasbourg, France, 26-30 May 2008
  http://www.emrs-strasbourg.com/

2008 saw the 25th anniversary of the E-MRS and an ESF–EUROCORES–SONS II symposium was organised as part of the E-MRS 2008 Spring Meeting in Strasbourg. Mario Ruben, Paolo Samori (project leaders of SUPRAMATES and FUNSMART II, respectively) and Franco Cacialli (principal investigator, SUPRAMATES) co-chaired the symposium entitled "Functional Supramolecular Architectures for Organic Electronics and Nanotechnology", together with Giovanni Marletta (University of Catania, Italy) and Roberto Faria (University of São Paulo, Brazil). A crowded lecture hall warmly welcomed Professor Jean-Marie Lehn, Nobel Laureate in Chemistry 1987, who gave the opening talk. Throughout the meeting, the most challenging aspects of the field were discussed in 17 sessions, with a total of 47 contributed talks covering synthetic chemistry, molecular self-assembly, interface studies, advanced imaging and processing at the nanoscale, and spectroscopy of supramolecular assemblies. A strongly multidisciplinary symposium took place with world-class speakers, to a great extent from SONS II CRPs, including Richard Friend (SUPRAMATES), Klaus Müllen (SUPRAMATES), Alessandro De Vita (FunSMARTs II) and Johannes Barth (FunSMARTs II), who reviewed the current state of their respective areas of speciality and suggested guidelines for the development of scientific research in supramolecular science and nanotechnology. Looking to the future, a significant amount of time was dedicated to the next generation of material scientists with two poster sessions that saw the participation of more than 250 young investigators, a large number of whom were associated with SONS II projects. The high quality of the projects and timeliness of the symposium was reflected in the support secured from the top-class journals *Nature Materials* and *Advanced Materials*, sponsoring awards for *Most Original Research Work*, *Most Promising Young Investigator* and *Best Poster.* In addition, Inchan Hwang (University of Cambridge, UK) and Anna Llanes-Pallas (University of Trieste, Italy) were awarded with E-MRS Graduate student awards. These are given to students in recognition of "exceptional ability who show promise for significant future achievement in materials research". As a follow-up, the proceedings of the symposium were published in the high-ranked journal *Advanced Materials* (Wiley-VCH) in early 2009.

- **Workshop on Self-Organised Nanostructures in Liquid Crystals**
  Cetraro, Italy, 15-18 September 2008

This workshop was held to discuss the current state-of-the-art in synthesis, analysis, characterisation, computer modelling and materials properties evaluation of liquid crystalline systems, particularly those leading to self-organised nanostructures not commonly observed for bulk low molar mass liquid crystals. The participants were mainly from SCALES and LC-NANOP. However, members from other CRPs were also welcome and took part as both invited speakers and regular participants. In total, 44 researchers attended the meeting.

The meeting consisted of both oral and poster presentations, and started with an introduction to the ESF programmes from Antonella di Trapani (ESF), and to the two liquid crystalline based networks from their project leaders. After this first session all talks were research based; 20 were given by members of LC-NANOP and SCALES with an additional four longer ones by the invited speakers from other CRPs. Just over 50% of the talks were given by young researchers.

In addition to SONS II members, Sergei Chvalun (Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Russia) was invited to speak on X-ray characterisation of (non-liquid crystalline) self-assembling organic molecules. The X-ray characterisation techniques used in his group complement those in SCALES, and this led to discussions about improving the data achievable in liquid crystalline self-organised structures within the network.

The majority of the talks from the SCALES groups were based on bolaamphiphiles; these covered the synthesis, X-ray structure determination, properties and modelling of the various phases that this class of molecules can exhibit. Talks from LC-NANOP covered the liquid crystalline behaviour of, for example, functionalised gold and iron oxide nanoparticles, dendrimers and colloidal particles. In addition to the talks, a sufficient amount of time was available for scientific discussion outside the formal lecture structure. This included possible future collaborations and grant proposals/funding sources. At least one proposal has been submitted based on discussions arising at this symposium from members of LC-NANOP and SCALES.

- **Workshop on Magnetic Nanostructures on Surfaces**
  Baden-Baden, Germany,
  28 September–1 October 2008

The goal of this workshop was to strengthen the interaction and exchange between two scientific communities dealing with magnetic objects at surfaces, a dynamic research field. In SONS II, the two communities were represented by members of FunSMARTS II, who are in particular practised in handling magnetic molecules, and SANMAG, who are very experienced in the deposition and surface characterisation of magnetic cluster objects. Although the participants had differing scientific backgrounds, the considerable scientific overlap that exists between their research fields was expected to provide the basis of mutual discussions. In this spirit, the 2007 winner of the Nobel Prize in Physics, Professor Peter Grünberg (Jülich Research Centre, Germany), opened the conference with a very enthusiastic talk dealing with thin layer magnetism. Being at the borderline of open surface and nanoscale magnetism, he introduced perfectly the topic of the workshop.

The links between the scientific fields were underlined during the meeting as the topics discussed moved smoothly from molecular magnetism, to self assembly of both molecular magnets and magnetic metal ions on surfaces, to the magnetic characterisation of nano-objects and their mobility on surfaces. The relevance of the work for biological applications and quantum computing was highlighted. Other areas covered at the meeting were the spin dynamics of low-dimensional magnetic systems and electronic transport through magnetic systems. The latter topic includes a new type of strongly coupled interaction and is also very important for possible applications. There were 40 delegates at the workshop and 12 posters were presented.

- **ICAM 2009 – 11th International Conference on Advanced Materials**
  Rio de Janeiro, Brazil, 20-25 September 2009

The ICAM conference is among the most worldwide relevant initiatives in the field of organised materials. It is one of the prestigious conferences of the International Union of Materials Research Societies (IUMRS) and is held in alternate years. ICAM 2009, held in Rio de Janeiro, Brazil, had 28 technical symposia, four plenary lectures, an Energy Forum and an exhibition. Each symposium had invited and contributed talks, and poster presentations. A range of topics at the frontiers of material research of contemporary importance for science, technology and engineering were highlighted including materials for nanotechnology, health, energy, environment; functional, electronic and structural materials; theory and phenomena, as well as topics of general interest including education and theoretical and experimental approaches to materials engineering. Many distinguished scientists were present, delivering plenary and invited talks, among more than 1500 delegates. As such, it provided an ideal outlet to disseminate the scientific findings developed in the frame of SONS II.

The symposium on "Functional Materials For Organic Electronic and Nanotechnology" organised by Paolo Samori, project leader from SUPRAMATES, was one of the most highly attended symposia. It provided the opportunity for all seven SONS II CRPs to present and discuss the results of their work. Invited talks were given by Franco Cacialli (SUPRAMATES), Mario Ruben (FunSMARTs II), Mukundan Thelakkat (SOHYD), Ewa Gorecka (LC-NANOP), Helmut Schlaad (BIOSONS), Jan Honolka (SANMAG), and Martin Bates (SCALES).

- **SONS II Final Conference**
  Prague, Czech Republic, 19-22 October 2009
  http://www.imc.cas.cz/sympo/sons2009/

The purpose of this conference was to gather researchers active in SONS II projects in the fields of both soft matter and hard matter research, to provide an avenue for presenting results obtained within these projects, to share general ideas on self-organisation of matter, and promote the continuing cooperation of various scientists taking part in these activities in the future. The meeting was held at the Institute of Macromolecular Chemistry in Prague and had 80 participants, the majority of whom were members of various projects within the SONS II programme. A total of 33 lectures were given over nine technical sessions, including those of five external researchers – Rasmita Raval (University of Liverpool, UK), Ian Manners (University of Bristol, UK), Julius Vancso (University of Twente, the Netherlands), Walter Richtering (Aachen University, Germany) and Tadahiro Komeda (Tohoku University, Japan) – who were invited to introduce the various topics addressed at the meeting. As well as the talks, 38 posters were presented and opportunities for further collaboration and networking activities facilitated by the ESF were discussed.

The conference reviewed the most important achievements in the field of self-organisation of soft and hard matter during the SONS II programme, and emphasised the most challenging problems and links between fundamental research and the related nanotechnological applications. In the field of soft matter the subjects discussed were in the complementary domains of polymer, biopolymer, colloidal and liquid crystal research. In the area of surface-confined organisation of molecules, experimental and theoretical activities were presented that promote the understanding of the self-organisation, interaction and steering of nanoscale (supra) molecular systems (e.g. molecules, metal centres, nanoparticles) at surfaces. The common aspect of all the approaches reported, including advanced methods for studying structural and dynamic properties, is the self-organisation that the researchers exploit in order to reach a particular technical application or to acquire an understanding of the underlying physical and physico-chemical principles that are required to lay solid grounds for a particular practical application.

In addition to the technical sessions, and in line with the goal of sustaining and developing collaboration between the CRPs, time was devoted to reflect on the nature of the programme and its effects. The discussions pointed at the great benefit that all participating research groups acquired from being involved in the programme in terms of new scientific achievements and establishing and strengthening international collaboration in the respective fields. It was felt that the cross-disciplinary approach of the programme was proven to be particularly useful because researchers with different backgrounds, yet similar interests, could share many scientific issues they have in common but had been addressing with different approaches. From this point of view it was concluded that the EUROCORES scheme and the network facilities it provides are a very useful way of generating synergy in research in one of the very important fields in the science of nanotechnology.

- **Workshop on Functional Multiscale Architectures**
  Bologna, Italy, 5-7 May 2010
  http://www.isof.cnr.it/funmarch/

With the aim of providing a forum for an extensive and final summary of the achievements obtained in the frame of SONS II, this workshop was jointly organised by members of the SUPRAMATES (Paolo Samorì, Vincenzo Palermo) and FunSMARTS II (Fabio Biscarini and Massimiliano Cavallini) CRPs near the end of the programme. Overall the workshop addressed the key question in functional nanostructure, i.e. unravelling the structure vs property relationship in nanomaterials. It focused on the self-assembly of supramolecular architectures of interest for various technologically relevant applications. These included organic (opto)electronics and spintronics, as well as the broader realms of bio-nanotechnology, catalysis and nanomedicine. Particular emphasis was given to the supramolecular approach because the ability to manipulate the local molecular environment is crucial to access fundamentally new classes of functional materials with unprecedented properties and performance. Experienced researchers, post-docs and PhD students from all over Europe who contributed to SONS II were invited to participate in the workshop which was also open to those not directly linked with SONS II projects. The topic was clearly of significant interest as attendance was higher than expected with 86 scientists participating, a considerable number of whom were not partners of SONS II projects. Furthermore, the workshop attracted the sponsorship of three international publishers, Nature Publishing Group, the Royal Society of Chemistry and Wiley, that provided poster awards for young scientists. Delegates represented five of the SONS II CRPs (BIOSONS, FUNSMART II, LC-NANOP, SCALES, SUPRAMATES), as well as one of the SONS I CRPs (BIONICS) and one of the Fundamentals of Nanoelectronics, FoNE, CRPs (DEWINT). During the workshop there were 22 oral presentations, 40 posters, nine invited talks and two talks on research funding (from ESF and ERC representatives).

The ultimate goal of the workshop was not only to provide to both researchers and ESF with an overview of what has been done within all the SONS II CRPs but, most importantly, to use this overview as a tool to evaluate the most promising research directions in the fields of self-organised materials, and in nanotechnology in general. In this frame, the final session of the workshop was dedicated to talks dealing with research on graphene, to create an ideal link and a scientific continuity between SONS II and the ESF EUROCORES programme EuroGRAPHENE, which was launched shortly after the workshop.

Frontiers of Chemistry:
From Molecules to Systems
A One-Day Symposium

Celebrating 10 Years of

On 21st May 2010 in Paris
at the Maison de la Chimie
(near the Eiffel Tower and Les Invalides)

Speakers

Gerhard Ertl
Nobel Prize 2007

Jean-Marie Lehn
Nobel Prize 1987

Roger Y. Tsien
Nobel Prize 2008

Ada Yonath
Nobel Prize 2009

Luisa De Cola

Alan R. Fersht

Marc Fontecave

Michael Grätzel

Michel Orrit

Nicolas Winssinger

Scientific committee
E. Amouyal, M. Che,
F. C. De Schryver,
A. R. Fersht, P. Gölitz,
J. T. Hynes, J.-M. Lehn

Posters
will be displayed also online from 1st April.

www.chembiophyschem.org

Topics
catalysis, biochemical imaging,
chemical biology, bionanotechnology,
proteomics, spectroscopy, solar cells

- **Symposium of Chemistry: From Molecules to Systems (SONS II Poster session)**
  Paris, France, 21 May 2010
  www.chembiophyschem.org

The one-day symposium "Frontiers of Chemistry: From Molecules to Systems" was organised by Wiley VCH in the occasion of the celebration of the 10th anniversary of journals *ChemPhysChem* and *ChemBioChem*. Upon invitation by Peter Gölitz, editor of Wiley-VCH, eight young scientists (PhD students and postdocs) from SONS II presented the work carried out within their CRP during the poster session. All seven SONS II CRPs were represented as follows: Andrea Liscio (SUPRAMATES), Svetlana Klyatskaya (FunSMARTs II), Joke Vandenbergh (SOHYD), Abdelhak Belaissaoui and Mirek Salamo'nczyk (LC-NANOP), Patrick Baumann (BIOSONS), Aitor Mugarza (SANMAG), and Lui Feng (SCALES).

Plenary lectures were given by ten eminent chemists including four Nobel Laureates in Chemistry: Gerhard Ertl (2007), Jean-Marie Lehn (1987), Roger Y. Tsien (2008) and Ada Yonath (2009). The event brought together more than 600 participants and over one hundred posters in the areas of physical chemistry and biochemistry were presented offering junior researchers many opportunities for dialogue. The visibility of SONS II and ESF at the event was further enhanced with a booth that attracted a very large number of visitors during the breaks. Attendees were particularly interested in EUROCORES and Research Networking Programmes.

Other events include participation in the Materials Research Society Fall Meeting, Boston, USA, 1st–5th December 2008; a two-day meeting in Ljubljana, Slovenia; a three-day meeting in Halle, Germany; and a three-day international conference at Falenty, Poland. The meeting in Falenty was particularly fruitful in that it brought together a large group of experimental chemists and materials scientists with a large local group of physicists, leading to the crystallisation of a number of important ideas arising from experimental results.

5.

Impact and Outreach Activities

● ● ●

5.1 Patents

SCALES

Sposób przyspieszania separacji faz w układach niejednorodnych, zwłaszcza w układach polimer/ciekły kryształ i polimer/polimer. (Method for speeding up phase separation in non-uniform systems especially in polymer/liquid crystal and polymer/polymer mixtures.)
Hołyst, R., Garstecki, P., Wieczorek, S., Szymborski, T. and Natalia Ziębacz, N.
Polish Patent Office patent application: P-385743 (2008).

SOHYD

A hybrid organic light emitting device.
Haque, S. A. and Bradley, D. D. C.
Application no.: PCT/GB2007/002657
Publication no.: WO/2008/007124

Tri-tert-butylcarboxyphthalocyanines, uses thereof and a process for their preparation.
Torres-Cebada, T., Cid-Martin, J. J., Nazeerudin, Md. K., Yum, J. H., Graetzel, M. and Palomares, E.
Application no.: PCT/EP2007/055110
Publication no.: WO/2008/145172

BIOSONS

Biopolymer, implant comprising it and uses thereof
Rodríguez-Cabello, J.C., Alonso, M., Arias, F. J., Girotti, A., Martin, L. and Testera. A. M.
Application no.: PCT/ES2010/070084
Publication no.: WO/2010/092224

Metallic functionalized nanoparticles that make up a system that is sensible to pH, temperature and UV-vis radiation variations.
Alvarez, R., Rodríguez-Cabello, J.C., Santos, M., Alonso, M., Arias, F. J. and Testera. A. M.
Application no.: P200900418
Application date: 13.02.2009

New recombinant elastin-like protein polymers and a method of surfaces bioactivation with such polymers.
Conrado, J. A., Planell, J. A., Salvagni, E., Werner, M., Gil, F. J., Rodríguez-Cabello, J. C., Alonso, M., Arias, F. J., Girotti, A. and Ribeiro, A.
Application no.: P200900418
Application date: 29.09.2009

5.2 Related European Research Council grants

5.2.1 Advanced Investigators grant

- Johannes V. Barth (FunSMARTs II)
  2009
  MOLART – Surface-confined metallosupramolecular architecture: towards a novel coordination chemistry for the design of functional nanosystems.
- Klaus Müllen (SUPRAMATES)
  2010
  NANOGRAPH – The chemists way of making and utilising perfect graphenes.
- Eugenio Coronado Miralles (SOHYD)
  2009
  SPINMOL – Magnetic molecules and hybrid materials for molecular spintronics.
- Michael Grätzel (SOHYD)
  2009
  MESOLIGHT – Mesoscopic junctions for light energy harvesting and conversion.

5.2.2 Starting Independent Researcher grant

- Partner Pietro Gambardella (SANMAG)
  2007
  NOMAD – Nanoscale Magnetisation Dynamics.
- Paolo Samorì (SUPRAMATES)
  2010
  SUPRAFUNCTION – Supramolecular materials for organic electronics: unravelling the architecture vs. function relationship.

5.3 Press Releases

- "Blaues Licht für flache Schirme" (SUPRAMATES)
  http://www.mpip-mainz.mpg.de/www/pages/aktuelles/pressemitteilungen/?year=2008#kap_59
  10.12.2008
- "Hochempfindlicher Sprengstoffschnüffler zum Mini-Preis" (SUPRAMATES)
  http://idw-online.de/pages/de/news274062
  15.08.2008
- "Evolution in the Nanoworld" (FunSMARTs II)
  Press Release T/2007(167), KIT Karlsruhe/Max Planck Society, 30.10.2007
- "Nanoscale Switching" (FunSMARTs II)
  KIT-Wiley, December 2008
- "Datenspeicher gehen ins Netz" (FunSMARTs II and SANMAG)
  MPG Press Release C/2009 (37), 16.03.2009
- "The Royal Society of Chemistry Interdisciplinary Award to Prof. J. W. Goodby" (LC-NANOP)
  http://www.york.ac.uk/admin/presspr/pressreleases/leyseraward.htm
  17.05.2007
- "Web Search Leads to Award-winning Collaborative Work" (LC-NANOP)
  http://www.esf.org/media-centre/ext-single-news/article/web-search-leads-to-award-winning-collaborative-work-332.html
  04.10.2007
- "Delikate Beziehungen zwischen einzelnen Spins -Wissenschaftler messen die magnetische Wechselwirkung zwischen einzelnen Atomen" (SANMAG)
  MPG Press Release C/2007 (24), 26.02.2007
- "Den Weg zu Speichermedien im Nanoformat geebnet" (SANMAG)
  MPG Press Release C/2009 (41), 19.03.2009

5.4 Interviews and Articles in Printed and Online Newspapers/Journals

- "Dupont science prices for N. Martín" (SOHYD)
  Angew. Chem. Int. Ed. **47**, 30 (2008)
- "Chaining up Fullerenes" (SOHYD)
  Chemical and Engineering News, 03.02.2008
- "El futuro de la Energia solar está en sus manos" (SOHYD)
  Tribuna Complutense, 03.05.2007
- "La calidad de la investigación química" (SOHYD)
  El País, 29.09.2004
- "La mejor alternativa a los paneles solares de silicio serán las células de plastic" (SOHYD)
  La Razón, Suplemento Verde, 03.02.2008
- "Espanya ya ficha los cracks de la scienta" (SANMAG)
  La Vanguardia, 07.04.2008
- "Studies put us on track for new magnetic phenomena and materials" (SANMAG)
  Diamond News, Autumn 2009
- "Grid allows manipulation of magnetic moments" (SANMAG)
  K. Oliver, *ESRF News* **50**, June 2009
- "Pushing the superparamagnetic limit" (SANMAG)
  Physics, December 2008

5.5 Other Outreach Activities

- **Thermogelating video**: http://www.youtube.com/watch?v=dPDmVXZHDBw

6.

Related ESF Activities

This section provides a summary of activities related to the field of self-organising nanostructures that have recently taken place or are currently ongoing at ESF.

6.1 Research Networking Programme: ORGANISOLAR

New Generation of Organic Based Photovoltaic Devices

Solar energy conversion based on organic materials is an emerging research field with substantial future prospects. A broad range of distinct device technologies are currently being developed, including dye-sensitised nanocrystalline solar cells, polymer/fullerene blends, small-molecule thin films and hybrid polymer/nanocrystal devices. Several European groups have already established themselves as world leaders in this field with, for example, world-record efficiencies for both dye-sensitised and polymer/fullerene devices currently being held by research groups in Lausanne and Linz respectively. Major nationally based research programmes are underway with extensive European industrial investment. At present the field is developing diversely across Europe, with different national programmes tending to focus on different technologies. In particular, the two largest communities in this field, namely dye-sensitised nanocrystalline devices and polymer-based devices, have to date developed and functioned largely independently with few overlaps. This division is, however, becoming a growing barrier to development of the field, with scientific progress increasingly being made in device concepts which lie at the intersection of these two research communities.

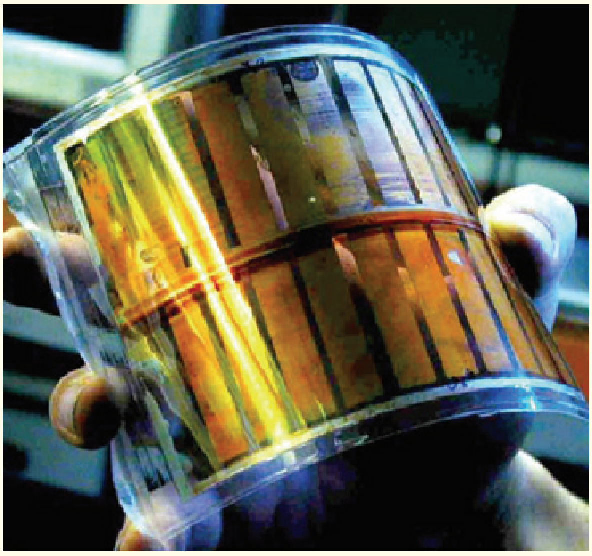


Figure 10.
Plastic organic solar cells (LIOS). Photo and device scheme

ORGANISOLAR aims to bring together these diverse research programmes across Europe and develop a cohesive pan-European research community targeting the development of innovative, low cost, organic-based photovoltaic cells. The programme is positioned at the intersection between solid state physics, chemistry and materials science, and the specific goals are summarised as follows:

- to boost the efficiency of an all solid state solar cell further from the present to >8% as a result of increasing interactions and joint collaborations via scientific meetings, and knowledge, know-how and person transfer;
- to integrate European research and development activities within chemistry, materials science, photophysics and device physics in the field of organic semiconductors. Through this interdisciplinary integration, European leadership in the field will be further established for the future;

- to integrate European research and development activities within the two largest communities in this field, namely dye-sensitised nanocrystalline devices and polymer-based devices that have to date developed and functioned largely independently. A better knowledge of the advances made in the whole community of organic-based solar cells will help to establish faster and more important progress in that field;
- to disseminate these excellences in research and development to European industry, so that the leadership of European-based technology in the field of organic solar cells will have a better impact on the worldwide scene.

ORGANISOLAR is running for five years from September 2006 to September 2011.

6.2 Research Networking Programme: INTELBIOMAT

Interdisciplinary Approaches to Functional Electronic and Biological Materials

INTELBIOMAT is a European programme of workshops, schools, and exchange visits targeted at the understanding, modelling and design of functional materials. Materials functionality is often based on phenomena that are poorly understood at a predictive level either because of inherently strong interactions (e.g. magnetism, ferroelectricity, superconductivity) or complex structure (e.g. composites, oxides, biomaterials), and increasingly both. There are three distinct paths that now offer the possibility to move forward in fundamental understanding and eventual design of materials: novel theoretical methodologies, improved materials control, and advanced experimental techniques. INTELBIOMAT will exploit and enhance the high level of local investment with a European dimension. At the same time by working jointly with an established (and US National Science Foundation-funded) programme, the European network will acquire an international dimension across North America and Asia.

By bringing together experimentalists and theoreticians with different research backgrounds INTELBIOMAT will address the following scientific challenges:

- new theoretical methods for strong correlations;
- excited states;
- advanced spectroscopies and computational spectroscopy;
- modelling materials with complex structures;
- materials with new or improved functionalities.

Areas considered:

- oxides with novel electronic properties: cobaltates (thermoelectrics), cuprates (superconductors), ferromagnetic and multiferroic oxides (spintronics);
- rare-earth and actinide compounds: rare-earth-based pigments, and phosphors for solid-state lighting, heavy fermion compounds with novel fundamental properties;
- structure and modelling of biomaterials and biologically active molecules, receptor "design", supra-molecular assembly, sensing;
- organic electronic materials including crystalline, glassy, and polymeric materials;
- low-dimensional structures and carbon-based nanostructures;
- transport and optics in nanostructures, quantum dots, optical microcavities, inorganic/organic composites, and magnetic semiconductors.

INTELBIOMAT is running for five years from June 2008 to June 2013.
More information can be found at:
http://intelbiomat.org.

6.3 Research Networking Programme: P^2M

Precision Polymer Materials

P^2M aims to combine the complementary expertise of leading European research groups in the design of precision polymeric materials, i.e. polymers with precisely defined molecular weight, architecture and functionality, that are designed to self-assemble into functional materials via strategies that are inspired by or mimic biological self-assembly processes. More specifically the design and synthesis –through sustainable polymer chemistry methodologies – of new functional polymers with self-assembling and/or templating properties towards nanostructured materials, material systems and devices using simple processing methods. The ultimate goal is to design new functional polymer materials and processes for future information and communication, energy, life science and environmental technologies. As well as this, it will promote interactions and facilitate exchange between, primarily, early career researchers with different backgrounds, ranging from catalysis, polymer chemistry and physics to theory, biochemistry and pharmacy. The intention is to train highly skilled people who will be joining either academia or traditional and high technology industries, or will be contributing in creating new high-tech industrial sectors.

The three main scientific objectives of P²M are:

- precision polymer synthesis – new approaches in polymerisation catalysis, controlled polymerisations for defined polymeric architectures, hybrid polymer–biological polymer systems;
- controlled and directed self-assembly – self-assembly via supramolecular interactions, peptide and protein-based self-assemblies, DNA-based self-assemblies;
- (multi)functional polymer materials – drug delivery systems, surface active materials, nanoreactors, bio-electronic polymer materials.

P²M is running for five years from July 2011 to July 2016. More information can be found at:
www.esf.org/p2m

6.4 EUROCORES Programme: EuroGRAPHENE

Maximising the Impact of Graphene Research in Science and Innovation

EuroGRAPHENE is a three-year programme which recognises that there is a clear need for European-wide cooperation to tackle the challenges of deepening current understanding of the physical properties of graphene; expanding research into new areas of chemically modifying the material and searching for methods to design its electronic properties; investigating its mechanical and electromechanical properties, broadly studying kinetic processes in graphene aiming at understanding optoelectronic effects; and modelling graphene-based devices for any functional applications.

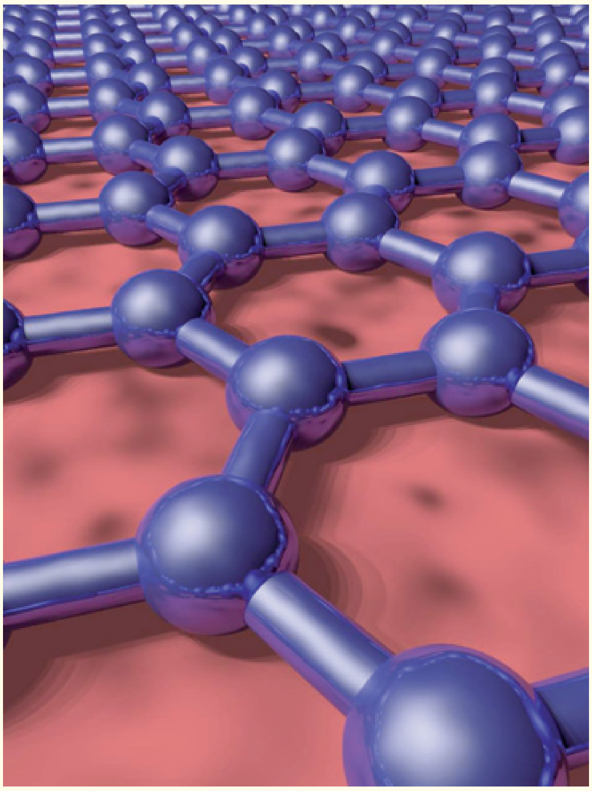


Figure 11.
The physical structure of graphene consists of a single layer of carbon atoms densely packed in a honeycomb crystal lattice (Courtesy of V. Palermo, ISOF, Bologna, Italy).

EuroGRAPHENE provides the framework for bringing together the complementary expertise of technologists, experimentalists and theorists within small and medium-size consortia of world-leading European research groups. In doing so it aims to accelerate the pace of European research in graphene and its applications by concentrating and networking the activities.

The EuroGRAPHENE EUROCORES Programme will run for three years from June 2010 to June 2013. More information can be found at:
www.esf.org/eurographene

6.5 EUROCORES Programme: EuroSolarFuels

Molecular Science for a Conceptual Transition from Fossil to Solar Fuels

Europe depends heavily on outside energy resources. In particular this concerns fossil fuels which have severe availability constraints, pollution problems and emit large amounts of CO_2, linking them to global warming. As a consequence, environmentally friendly fuel production is of strategic importance for both medium- and long-term research; a strong need is felt for heavy development of and investment in solar energy research. The vision is that extensive development and increased use of solar fuels shall be a major path to follow to alleviate the effects of climate change caused by extensive use of fossil fuels.

Huge amounts of solar energy are available everywhere and are often abundant where the population is dense. Even in northern Europe there is enough solar energy to contribute substantially to the energy system in the summer months because of the many hours of daylight. However, it is lacking in winter when energy demand is high. If this abundant solar energy could be converted into a storable energy carrier (fuel), solar energy could become an important energy source for all countries throughout the year.

The aim of EuroSolarFuels is to develop molecular science to produce a CO_2-lean solar fuel to accomplish the grand challenge of phasing out fos-

sil fuels. All parts of the programme aim for direct conversion of solar energy in the visible part of the spectrum to chemical energy – a fuel. It focuses on water as the electron source and includes photobiological solar fuel production in green algae and/or cyanobacteria that excrete the fuel, artificial photosynthesis in molecular systems and solar fuel production in nanostructured and semiconductor-based systems. To meet these goals, EuroSolarFuels has the ambition of developing solar fuels research into a powerful field in Europe by bringing together all European scientists active in relevant disciplines. More information can be found at:
www.esf.org/eurosolarfuels

6.6 Exploratory Workshop: Bacterial Protein Dynamic Scaffolds for Fabrication of Self-Organised Nanostructures

Madrid, Spain, 20-23 February 2011

The main objective of this exploratory workshop was to bring together scientists with different research backgrounds to initiate a long-term solid collaboration aiming to develop a synthetic platform based on bacterial proteins to manufacture self-assembling nanocomposite materials. The use of biomolecules as scaffolds for the synthesis of smart self-assembling nanocomposite materials offers important advantages: an alternative to existing manufacturing protocols that involve harsh temperatures, radiation, or pressure conditions used in standard lithographic techniques that limit the incorporation of active organic or biological materials into nanodevices, self-organising capacity at room temperature in aqueous conditions and potential control over shape and distribution through external stimuli.

The workshop integrated multidisciplinary academic groups and industrial companies from Europe and Israel to explore the fabrication of novel smart organic–inorganic hybrid materials using self-assembling bacterial cytoskeletal proteins and amyloid proteins as scaffolds for mineralisation and chemical modification. The bacterial proteins can be genetically engineered to carry different organic or inorganic ligands that then assemble guided by the self-organising properties of the protein scaffold. These hybrid nanostructured materials have the potential to combine electronic, mechanical, optical, or ligand-binding capacities to facilitate cross-talk between different functionalities to develop multifunctional self-assembling nanodevices.

There were 14 participants at the workshop whose interests and expertise included:

- molecular biology, to genetically modify the bacterial proteins;
- nanotechnology, biochemistry and biophysics, areas required to characterise and control the process of protein assembly and the properties of the aggregates formed;
- semiconductors and biosensor development, to provide tools to integrate these novel materials within devices.

The workshop consisted of presentations of participants' recent results and sessions dedicated to establish how the partners could work together to contribute to the future of the field. Most of the participants had not previously interacted with each other and the relaxed nature of the workshop played a large part in fostering scientific exchange. The fruitful discussions produced many actions including plans to write a position paper and apply for FP7 funding, as well as practical ideas for laboratory experiments.

7.
Conclusions

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SONS II received a very positive final review by the Review Panel, who commented in the final report that SONS II "*has been very successful in bringing together world-class research groups and in producing high level and innovative scientific achievements.*" The high calibre of researchers is reflected in the number of European Research Council grants that have been awarded to participants of the programme.

The seven CRPs covered a broad range of scientific topics within the area of supramolecular approaches to functional materials and generated a substantial amount of both fundamental and applied knowledge. The programme enabled different communities, each with their own expertise, to pool and enhance their resources thus creating conditions for the stimulation of research activities throughout Europe. All participants made excellent use of this which had a very positive impact on the various topical domains under examination. Networking activities played an important role in improving information sharing and facilitating a high number of common publications. Indeed the collaborative SONS II activities had a significant impact on the fundamental research, and the many achievements of the CRPs were made possible because of the numerous symposia that were organised, extensive exchanges, sharing of resources and complementary expertise.

Dissemination of the research results was deemed by the Review Panel to range from 'very good' to 'excellent' and it was naturally variable in nature. Researchers targeted high impact journals and gave an impressive number of invited talks and conference presentations; nevertheless the Review Panel felt that more could have been done to reach a wider audience. There were only a few examples where the excitement of the research activities was presented to the general public through press releases, TV appearances, and popular scientific communications. More of these outreach activities should be activated in order for the subject to gain and maintain the support of European citizens.

Overall, SONS II was a well organised and focused programme, succeeding in making a significant contribution to the European research portfolio. It brought together leading European researchers creating a fertile ground for the further development of innovative ideas. This stimulated a number of proposals for new national and EU programmes and international collaborations as well as laying the foundations for new nanostructured functional systems.

8.

EUROCORES Quality Assurance

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8.1 Theme Selection

New and challenging ideas for EUROCORES Programmes are invited from the scientific community through an annual Call for Theme Proposals. In addition to criteria including scientific quality, novelty and feasibility, the proposals are evaluated on the basis of the requirement for European collaboration: why it is necessary to conduct the programme at a European level and how the programme will strengthen and advance Europe's scientific position in a global context. Each proposal is sent for written external assessment to at least three referees. Based on these reviews, the Science Advisory Board (SAB) recommends which themes are to be further developed, a decision which is then ratified by the Governing Council.

8.2 Project Selection

The peer review of the CRP proposals in a EUROCORES Programme such as SONS II is a multi-stage process, including the establishment of an **international and independent Review Panel**. In response to an open call for proposals, **outline proposals** of about three pages are submitted by a team of applicants (minimum three from three different countries). At that stage, the Review Panel is responsible for the sifting of outline proposals prior to the invitation of full proposals. At the **full proposals stage**, each proposal is sent for **written external assessments** to at least three referees, including referees from outside Europe. Applicants are given an opportunity to reply to the anonymous referee reports.

Written referees' assessments and replies by applicants are then considered by the Review Panel with scientific quality being the main selection criterion. The Review Panel makes recommendations for funding of CRPs, with prioritisation, which ESF communicates to the EUROCORES Funding Organisations (EFOs).

After this international peer review process, which is managed by the ESF, seven CRPs were selected for SONS II. The CRPs encompassed 39 Individual research projects in nine different countries and were launched in December 2006.

8.3 Management Committee

At the time that the Call for Proposals is published, a Management Committee (MC) is established (see page 6).

- The MC has overall responsibility for the EUROCORES Programme within the guidelines of the EUROCORES Scheme;
- The MC can request expert advice from the EUROCORES Scientific Committee, Review Panel or any other *ad hoc* advisory group;
- Members support the EUROCORES review process by nominating potential Review Panel and external expert referees on behalf of their funding organisation;
- Each MC member is responsible for liaising with their funding organisation, including supervision of the funding process for EUROCORES projects within their organisation;
- Members may attend all meetings of the EUROCORES programme as observers.

8.4 Mid-term and Final Reviews

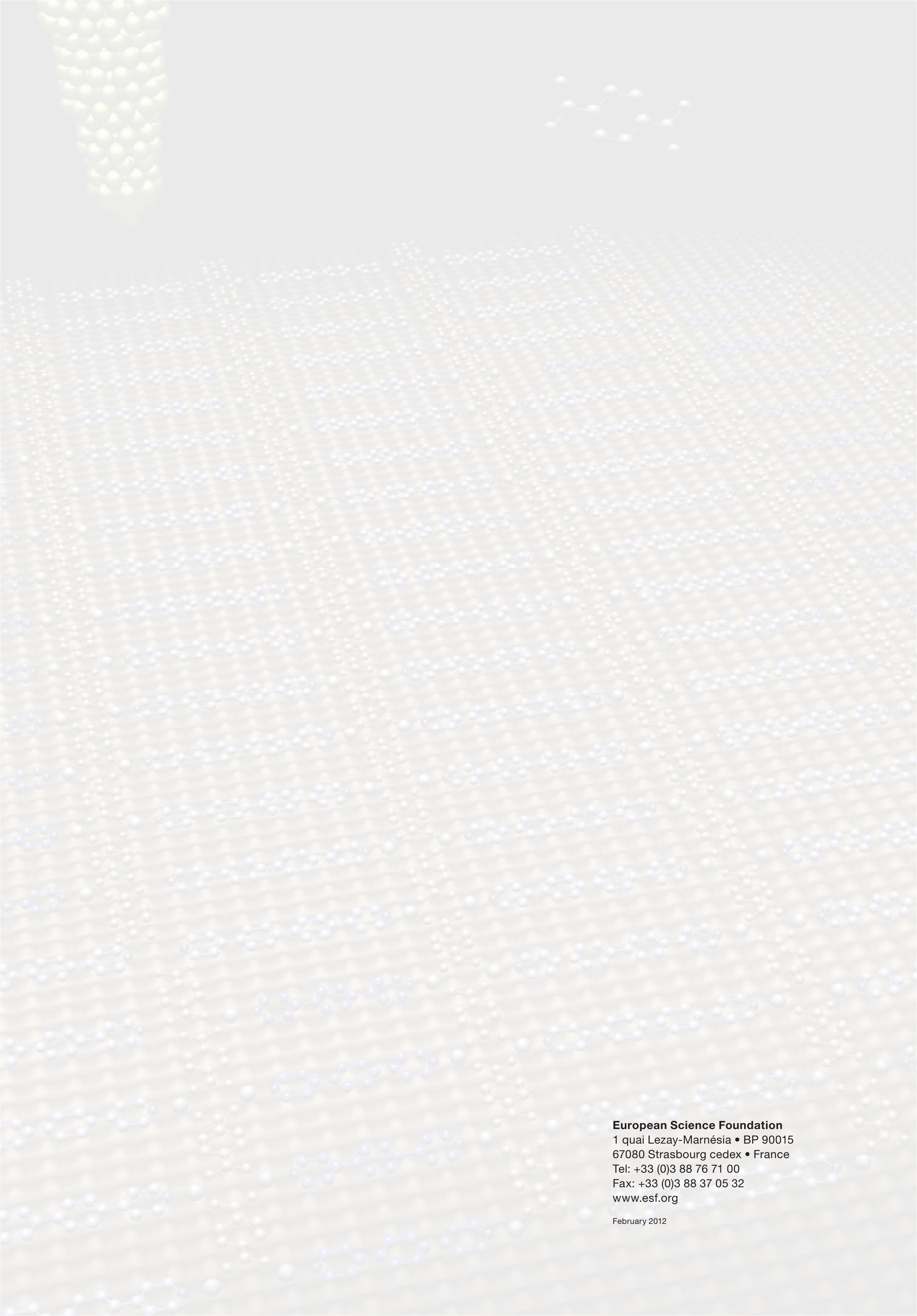
Each EUROCORES Programme undergoes two comprehensive reviews to evaluate its progress at the mid- and final stages. The aim is to assess scientific cooperation and interactions among the investigators and provide recommendations for the future.

The assessment is carried out by remote evaluation where the project leaders are asked to report on progress using the listed criteria:

- Novelty/Originality: Most innovative/original scientific contribution of each CRP to the programme and to the relevant field of research;
- Multidisciplinary Research: How is each CRP working towards (or achieving) multidisciplinary research;
- Collaborative Research: Results obtained within the CRP during this reporting period that would not have been achieved (or would have taken longer to achieve) in an individual project;
- European-added Value: European dimension given to national funding (e.g. building up ERA; developing a critical mass of expertise; addressing issues of scale and scope). For CRPs involving partners outside Europe: a clear example illustrating their added value to the programme and their contribution to the relevant field of research in Europe;
- Relevance to the Call: Achievement most relevant to the Call.

Based on these reports, the Review Panel is then asked to examine the scientific achievements, networking training and dissemination activities and assess the overall potential of the programme.

ISBN: 978-2-918428-62-6



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February 2012