EUROPEAN SCIENCE FOUNDATION
SETTING SCIENCE AGENDAS FOR EUROPE

EUROCORES Programme
European Collaborative Research

Self-Organised NanoStructures (SONS)

SONS FINAL REPORT

Assessment of SONS Programme by Review Panel
June 1st 2007, Strasbourg

1. Has Programme achieved goals as outlined in Call?

In our judgement, the programme has achieved the goals outlined in the call. By listening to talks at the mid-term and final conferences, and by studying the relevant reports, the review panel felt that most of the projects ran smoothly in a timely manner and achieved the expected competitiveness with other parts of the world.

This was most important, because at the outset of the programme, the panel members were worried that the combined evaluation and financing with national bodies would slow down progress to such an extent that priorities might be lost. Fortunately, the momentum and progress of the groups was sufficiently intense that no serious drawbacks were experienced.

- Have all topics been covered?

The programme covered a very broad spectrum of activities from theoretical physics to molecular biology. However, it is difficult to judge the extent of completeness of the coverage. Whereas the inter-disciplinarity of the programme was impressive and some areas were heavily represented, other areas of self-organizing science, e.g., from molecular biology and liquid crystals, were less well represented. This might reflect on the effectiveness with which the original calls were advertised.

- How did the various CRPs contribute to the Programme in terms of scientific output (e.g., to which extent a CRP advanced knowledge) and networking activities within and across CRP(s)?

In terms of scientific output, there were several projects that produced excellent publications in the top journals. Generally, the total number of publications across all of the projects was highly impressive, indicating that in terms of generating new science, the money was well spent. However, for some specific projects, the panel found that there was little evidence of the intended collaboration, suggesting limited co-operation between the laboratories. There are other criticisms of individual projects, such as under-delivery in terms of numbers/types of materials or in terms of the level of ambition of the project. Nevertheless, these should not detract from the overall effectiveness and success of the programme.

2. added value of the Programme within Europe

A critical mass of researchers was brought together within focussed collaborations in most of the projects. The synergies that emerged from these collaborations have contributed to the fostering and sustainable development of a leading role for European nanoscience in some key areas, e.g., self-organization of molecules on surfaces, optical tweezing, single molecule measurements, etc. Some of the results have potential value as IPR (Intellectual Property Right). It is

encouraging to see that some consortia and research topics were continued under SONS II or will move forward under Framework 7 (with industrial involvement).

3. impact & contributions of the Programme to the scientific field
   did Programme set new directions? Did it break new grounds?

The programme has helped to maintain and extend Europe's lead in certain fields and, within these, substantially pushed back the boundaries but did not establish new research fields or directions.

4. recommendations to ESF and funding agencies

Calls for new programme topics or for proposals should be better disseminated within the relevant scientific communities.

Also, it will be very crucial to secure a quicker start for newly approved projects.

Either a single-round process for proposal review and assessment should be considered or the first round filter should be handled in a quicker, more efficient, way.

a. for future developments of the Programme (target sub-area that was not covered? new directions that have emerged?...)

If SONS II were to be followed by SONS III, there are several scientific directions that would justify inclusion, e.g., molecular nano-photonics, plasmonics, biomimetics, biosensors, nanobiology, nanoscience for energy, etc.

b. for the future of the scientific field as a whole (mid-to long term vision to develop research agendas)

Nanoscience is an area in which Europe is strong and on which we must continue to build.

An important impact area for nanoscience will be the development of new materials and manufacturing processes that will minimize the environmental impact of new products and services, enhance the ease of remediation of waste and assist in realizing eco-technologies that facilitate environment management.

The future convergence of nanoscience with information technology, i.e., convergence of atoms and bits to achieve embedded intelligence, is a key emerging research domain.

Subsequent convergence between nanoscience, information technology and life science is important.

To move forward in these areas, it will be necessary to identify the appropriate human and infrastructural resources at the European level.

Reviewers: Richard Bushby, Joseph Gyulai, Pavel Kratochvil, Gareth Redmond on behalf of all the SONS Review Panel.

SONS FINAL REPORTS

EUROPEAN SCIENCE FOUNDATION	**EUROCORES Programme** European Collaborative Research **SONS** **Self-Organized NanoStructures**

Part 2

Final Report of the Collaborative Research Project "BIONICS"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number ():02-PE-SONS-008-BIONICS Acronym / Short Title: BIONICS Full Title: **BI**o-**O**rganics **N**anostructur**I**ng for molecular electroni**CS** Project Project Leader name: Prof. Dr. Klaus Müllen Project Leader affiliation: Max Planck Institut for Polymer Research, Mainz, Germany Institutional home page (URL): www.mpip-mainz.mpg.de Project-related home page (URL): http://bionics.bo.cnr.it Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator (name & affiliation): Prof. Dr. Klaus Müllen, Max Planck Institut for Polymer Research (MPI-Mainz), Mainz, Germany
Total Funding amount of the IP *(to be corrected by the PI)*
IP 2
Principal Investigator (name & affiliation):): Prof. Dr. Roeland J. M. Nolte, University of Nijmegen (KUNijmegen), Nijmegen, Netherlands
Total Funding amount of the IP *(to be corrected by the PI)*
IP 3
Principal Investigator (name & affiliation): Prof. Dr. Bruno Samori, Universita degli Studi di Bologna (Uni-Bo), Bologna, Italy
Total Funding amount of the IP *(to be corrected by the PI)*
IP 4
Principal Investigator (name & affiliation): Dr. Paolo Samori, Consiglio Nazionale

delle Ricerche (CNR-BO), Bologna, Italy
Total Funding amount of the IP *(to be corrected by the PI)*
IP 5
Principal Investigator (name & affiliation): Prof. Dr. Richard Friend, University of Cambridge (Uni-Cam), Cambridge, UK
Total Funding amount of the IP *(to be corrected by the PI)*
IP 6
Principal Investigator (name & affiliation): Prof. Dr. Frans De Schryver, Katholieke Universiteit Leuven (KU-Leuven), Leuven, Belgium
Total Funding amount of the IP *(to be corrected by the PI)*
AP 1
Principal Investigator (name & affiliation): none

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The aim of the collaborative research project (CRP) is to prepare complex bio-organic hybrid architectures with nanometer sized dimensions having pre-programmed shapes and functionalities. These materials are assembled in solution as well as on a surface. As scaffolds biological moieties such as nucleic acids or peptide based materials are employed. These supramolecular arrangements are decorated with small organic molecules, dyes, oligomers, or polymers either themselves pi-conjugated systems or containing a well defined number of pi-conjugated moieties. The final goal of the CRP is to to precisely nanopattern a surface with electrically or optically active molecules, and realizing novel molecular or (opto)electronic devices.

In the following the progress during the third year of the project towards these goals will be discussed. The best way to make the progress transparent in such a multidisciplinary undertaken is to consider the different steps towards the final task. These steps include: Preparation of biological scaffolds, synthesis of pi-conjugated systems, physical characterization of pi-conjugated moieties, preparation of devices, and the improvement of scientific instrumentation for studies of (bio)organic nanostructures.

<u>Preparation of biological and bioinspired scaffolds:</u>
In the course of the third year different biological scaffolds were synthesized, characterized and identified to act as persistent frameworks for a bottom-up approach towards more complex nanostructures. A novel class of DNA supramolecular polymers was introduced. These constructs are the result of the polymerization of a self-complementary 'monomeric' module. The parallelogram monomer can afford supramolecular polymers with different shapes when annealed under varying conditions (Uni-Bo). Beside using pristine DNA as building block also linear DNA block copolymers were synthesized. In the last year of the project single stranded building blocks could be assembled into multiblock copolymer architectures by hybridization. Moreover, DNA multiblock copolymer structures with extended nucleic acid segments were prepared by employing a technique from molecular biology, i.e. polymerase chain reaction (MPI-Mainz). A novel class of hybrid bio-organic 'comb-like' polymers were designed and synthesized. These comb like structures contain evenly-spaced nickel-nitrilo triacetic acid units along a polymer backbone (KUNijmegen).

<u>Synthesis of pi-conjugated systems</u>
During the third year of the CRP a wide variety of organic pi-systems has been achieved. Especially worth mentioning are fluorene and oligo fluorene derivatives that contain donor and acceptor groups within the same molecule (MPI-Mainz).

<u>Physical characterization of pi-conjugated moieties</u>
During the third year of the project nanographenes in combination with rylene dyes and isolated nanotubes of graphenes produced by a template approach have been studied by Scanning Force Microscopy techniques regarding their structural and/or electrical properties (ISOF-CNR).

Complementary to these experiments are photophysical measurements which have been performed on donor-acceptor-functionalized pentaphenylene model structures (Uni-Cam). Moreover, the optical properties and excited state dynamics of a perylene chromophoric nanowire system have been investigated via several techniques, such as time-correlated single photon counting (TCSPC) and transient absorption spectroscopy (Uni-Cam). Organic dye molecules used in a completely different context were studied in Leuven. With the help of these chromophores enzyme activity at the single molecule level was investigated intensively.

Preparation of devices

A new type of self-assembled DNA molecular device was designed synthesized and characterized (UniBo). The device is capable of responding to changes in pH of its environment by changing shape performing controlled movement on the nanometric scale, and is largely unaffected by steric constraints. The functioning of the device immobilized on a glass surface was also verified. The cycling of the device was confirmed at the single molecule level (KU-Leuven).
Beside the nanomechanical DNA device, the bioinspired isocyanopeptides containing stacked perylenes (KUNijmegen) were incorporated into solar cells. The optoelectronic devices containing these materials exhibited higher power output than reference cells without supramolecular order of dye molecules (Uni-Cam).
As biomedical devices a novel micelle platform consisting of amphiphilic DNA block copolymers was introduced for chemotherapeutic drug delivery, allowing for combinatorial testing of the drug carrier system. ODN-modified targeting units were "clicked" into the micelle corona by hybridization, allowing perfect control of surface functionalities of the nanoparticle system. Cancer cells were efficiently killed when targeting units and chemotherapeutic acted together within the DNA block copolymer drug delivery system (MPI-Mainz).

Upgrade and improvement of scientific instrumentation for study of (bio)organic nanostructures

The Unibo group felt that the Atomic Force Microscopes currently available on the market were not up to the task of characterizing the biomolecule-surface interactions studied in this project with the necessary precision. For this reason, a next-generation AFM was built, utilizing the best commercially available piezoelectric scanner and developing a custom real-time controller consisting of both hardware and software components. The instrument is tailored for constant-force 'force clamp' mechanical unfolding experiments. These experiments promise to be a direct way to probe the mechanical stability of elastic media at the nanoscale.

In summary, tremendous progress has been made in the third year of the CRP, BIONICS. Different biological scaffolds including nucleic acids and peptides with nanosized dimensions were prepared. Several conjugated pi-systems were synthesized and characterized regarding their electronic and photophysical properties. In the last period of the project the emphasis was put on the realization of devices. A working molecular device was realized in form of a pH dependent DNA nanomotor the action of which could be detected even on the single molecule level. In a second device application, bioinspired polymers with pi-conjugated perylene dyes have found successful application in solar cells. Finally, an easy to target drug delivery device based on DNA block copolymers was realized. These goals could only be realized by combining biological entities and organic molecules, in combination with sophisticated photophysical and morphological studies. Another prerequisite for realization of the scientific goals within the project was the setting provided by the Eurocores program. This allowed the close interaction of scientists of very different background on all levels from PIs over post docs to Ph.D. students.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

What was not achieved is an electronic device (nanobattery), based or partly based on bio molecules. The reason is that it took longer than expected to develop within the CRP the synthetic technology to construct architectures containing both proteins (or enzymes) and synthetic polymers. Now this technology is available the step to a nanobattery can be made. In this connection it is worth mentioning that we have received funding within the NanoNed programme of the Dutch government to continue this project.

Manipulation of the bio-organic structures on surfaces was not achieved because the equipment a combined optical microscope and scanning probe system was finalized only in the last part of 2006. Experiments along this line of research are presently executed.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

The consortium is continuing the research activity initiated in BIONICS, but with a greater emphasis on the materials for (opto)electronics rather than on bio(hybrid) systems, within the frame of ESF-SONS2-SUPRAMATES.
Moreover, the following FP7 proposals, which are a result of the collaboration of the CRP have been submitted: “Biocirc”, “Sensim”, “Success”, “Eurofet”.
Apart from collaborative research projects under FP7 the results achieved in BIONICS laid the foundation for proposals of the Eurocores 2 program BIOMATES, Marie curie programs and bilateral collaboration within national program IAP-VI (MPI-KU Leuven)

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

Within the ESF similar programs as Eurocores CRPs could be implemented for young researchers.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

- Access to new instrumentation and knowledge.
- Easier exchange of Ph. D students and post-docs.
- Implementation of long term research collaborations within Europe

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The Eurocores programme worked extremely well for us. No special comments to make.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

M.B.J. Otten, C. Ecker, G.A. Metselaar, A.E. Rowan, R.J.M. Nolte, P. Samori and J.P. Rabe, Alignment of extremely long single polymer chains by exploiting hydrodynamic flow, Chem. Phys. Chem. 5 (2004) 128

P. Samori, P.A.J. de Witte, R.J.M. Nolte, A.E. Rowan, H. Engelkamp, J.P. Rabe, Self-organization of semiconducing polysilixane-phthalocyanine on a graphite surface, Advanced Materials 17 (2005) 1265

P. Samori, F. Cacialli, H.L. Anderson and A.E. Rowan, Towards complex functions from complex materials, Adv. Mater. 18 (2006) 1235

P. Samorì, J.J.J.M. Donners, N. Severin, M.B.J. Otten, J.P. Rabe, R.J.M. Nolte, N.A.J.M. Sommerdijk, Tuning intermolecular interactions in a rod-like polymer assembled at surfaces and in solution, Langmuir 20 (2004) 8955

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H. Engelkamp, J. Hofkens, F.C. de Schryver, R.J.M. Nolte and A.E. Rowan, Do enzymes sleep and work?, Chem. Comm. 9 (2006) 935

M.B.J. Otten, G.A. Metselaar, J.J.L.M. Cornelissen, A.E. Rowan, R.J.M. Nolte, Polyisocyanides: stiffened foldamers, Book, in Ophir Flomenbom, Johan Hofkens, Kelly Velonia, Frans de Schryver, Alan E. Rowan, Roeland J. M. Nolte, Joseph Klafter, Robert J. Silbey, Correctly validating results from single molecule data: the case from single molecule data: the case of stretched exponential decay in the catalytic activity of single lipase B molecules, Chem. Phys. Lett. 432 (2006) 371

W. Zhuang, C. Ecker, G.A. Metselaar, A.E. Rowan, R.J. M. Nolte, P. Samorí, J.P. Rabe, SFM characterization of poly(isocyanodipeptide) single polymer chains in controlled environments: effect of tip adhesion and chain swelling, Macromolecules 38 (2005) 473

O. Flomenbom, K. Velonia, D. Loos, S. Masuo, M. Cotlet, Y. Engelborghs, J. Hofkens, A.E. Rowan, R.J.M. Nolte, F.C. de Schyver and J. Klafter, Temperal stretched exponential decay in the catalytic behaviour of fluctuating individual lipase molecules, Proc. Nat. Acad. Science 102 (2005) 2368

Kolaric B, Sliwa M, Brucale M, Vallée RAL, Zuccheri G, Samori B, Hofkens J, De Schryver FC, "Single molecule fluorescence spectroscopy of pH sensitive oligonucleotides switches" Photochemical & Photobiological Sciences 2007, [in press, DOI: 10.1039/b618689k]

P. Samorí, X. Yin, N. Tchebotareva, Z. Wang, T. Pakula, F. Jäckel, M.D. Watson, A. Venturini,

K. Müllen, J. P. Rabe, "Self-assembly of electron donor - acceptors dyads into ordered architectures in 2 and 3 dimensions: surface patterning and columnar "double cables"" *Journal of the American Chemical Society* **126**, 3567-3575 (2004).

F. Cacialli, P. Samorí, C. Silva "Supramolecular architectures for organic electronics and nanotechnology", (invited Review Article) *Materials Today* , **7** (4), 24-32 (2004)

P. Samorí, K. Müllen, J.P. Rabe, " Molecular scale tracking of the self-healing of polycrystalline monolayers at the solid-liquid interface", *Advanced Materials* **16**, 1761-1765 (2004).

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V. Palermo, M. Palma, Z. Tomovic, M. Watson, K. Müllen, P. Samorì "Supramolecular networks of π-conjugated discs on heterogeneous surfaces: effect of the micro- and nano-scale dewetting" *Synthetic Metals* **147**, 117-121 (2004)

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H.Uji-i, S.Melnikov, A. Beres, G. Bergamini, F.C. De Schryver, A. Hermann, K. Müllen, J. Enderlein, J.Hofkens Visualizing Spatial and Temporal Heterogeneity of Single Molecule Rotational Diffusionin a glassy Polymer by defocused Wide-field Imaging Polymer, 47, 2511-2518 (2006)

E Fron, T. Bell, A. Van Vooren, G. Schweitzer, J. Cornil, D. Beljonne, P. Toele, J. Jacob, K. Müllen, J. Hofkens, M. Van der Auweraer, F. C. De Schryver,
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Photochem.Photobiol.Sci., 2007, 6, 406-415

C. Flors, I. Oesterling, T. Schnitzler, E. Fron, G. Schweitzer, M. Sliwa, A. Herrmann, M. Van der Auweraer, F.C. De Schryver, K. Müllen, J. Hofkens
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J.Phys.Chem.C, vol. 111, n°12, 2007, 4861-4870

A.Margineanu, J.Hotta, R.A.L.Vallée, M. Van der Auweraer, M. Ameloot, A. Stefan, D. Beljonne, Y. Engelborghs, K. Müllen, F.C. De Schryver, J. Hofkens,
Visualization of membrane rafts using a perylene monoimide derivative and fluorescence lifetime imaging, Biophys. J. in press

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

M.B.J. Otten, C. Ecker, G.A. Metselaar, A.E. Rowan, R.J.M. Nolte, P. Samori and J.P. Rabe, Alignment of extremely long single polymer chains by exploiting hydrodynamic flow, Chem. Phys. Chem. 5 (2004) 128

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1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

A newspaper article was published in a Flemish newspaper on our single molecule studies carried out with the Leuven group. Frans de Schryver has the reference (de Standaard?)

Descartes Prize

1 D. Patents and industry collaborations

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Industrial colaboration: Novozymes

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

Progress meetings held every 6 months (final meeting was in Cambridge, Oct 2006)

Bilateral meetings with all the groups

Interactive materials exchange between several groups

1 F. Participation in other conferences

Please list only the most relevant

Zuccheri G, Brucale M, Samorì B, "DNA nanostructure adsorption and growth on inorganic surfaces" American Vacuum Society 53rd International Symposium 12-17 November 2006

Brucale M, Zuccheri G, Samorì B, "Linear and Circular Self-Assembled Supramolecular Polymers Made of DNA Parallelograms" 3rd Italian National Conference on Nanoscience and Nanotechnology Trieste 22-24 May 2006

Samorì B, "DNA absorption on Inorganic Surfaces and Nanostructure Growth" International Symposium on DNA-Based Nanoscale Integration Jena 18-20 May 2006

Dr. P. Samori

Chemistry and Physics of Multifunctional Materials-From Clever Molecules to Smart Materials Euroconference (ESF conference); Tomar, Portogallo, 11 - 16 September 2004

CERC3-workshop, Baden-Baden, Germania, 2-4 May 2005.

EMRS'05, Strasbourg, France, 31 May -3 June 2005

8th European Conference of Molecular Electronics, Bologna, Italia 29 June – 2 July 2005

"3rd National Conference on Nanoscience and Nanotechnology: The Molecular Approach" - Trieste (Italy) ; 21-23 May 2006

E-MRS 2006 Spring Meeting - Nice (France); 29 May- 2 June 2006

Royal Society Discussion Meeting on "Supramolecular nanotechnology for organic electronics"; London 5-6, June 2006.

ICN+T Conference - Basel (Switzerland); 31 July-4 August 2006

TNT 2006, Grenoble (France), 4-8 September 2006

3rd international meeting on Molecular Electronics (ELECMOL); Grenoble (France) 11-15 December, 2006.

Symposium on "Polymer Synthesis: the key to functional materials" honouring the 60th Birthday of Professor Klaus Müllen; Mainz (Germamy) 1-2 March 2007

4th NanoSpain Workshop; Sevilla (Spain) ; March 12-15, 2007.

F.C. De Schryver

5-9 januari, Mumbai/India : Biennial Trombay Symposium on Radiation & Photochemistry.

1-12 april, Kyoto/Japan : XXIst IUPAC Symposium on Phtochemistry.

Johan Hofkens :

20januari – 03 februari, San Jose Spie Congres: Bios 2006

19-24 maart, Eilat/Israel, Conference "Optical spectroscopy of biomolecular dynamics II"
Invited lecture "Single molecule enzymatics"

2-7 april, Kyoto : XXIst IUPAC Symposium on Photochemistry
. lecture : "Probing dynamics of individual biomolecules by single molecule spectroscopy

2-7 april, Kyoto : XXIst IUPAC Symposium on Photochemistry
lecture : "Probing dynamics of individual biomolecules by single molecule spectroscopy

6-8 juli, Japan Osaka : 3rd Intern.Nanophotonics Symp.
: *Lecture : Single molecule enzymatics*

3-8 Sept , Sapporo (Jap) : 16th Intern.Microscopy Congress (IMC16)

International conference on Synthetic Metals (ICSM), Dublin 2006

C.E. Finlayson et al. *Pentaphenylene All-in-One Materials*, poster 189-th

Dr. A. Herrmann
SONS Conference (European Science Foundation), Pisa, Italy June 2006

Transatlantic Frontiers of Chemistry Meeting, Durham, USA, August 2006

1st European Chemistry Congress (Euchem), Budapest, August 2006

SFB Meeting, Mainz, Germany, September 2006

Biomaterials, Hamburg, Germany, October 2006

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

Dr. J. Sly, post-doctoral fellow, 1-1-2005 to 1-7-2005
Dr. L. Ayres, post-doctoral fellow, 1-1-2005 to 1-4-2005
Dr. Nikos Hatzakis, post-doctoral fellow, 1-8-2005 to 31-12-2005
Dr. M. Koepf, post-doctoral fellow, 16-2-2007 to 15-2-2008

Marco Brucale, PhD student, Jan 2004- Dec 2006, achieved PhD in chemistry in 2007
Dr. Vincenzo Palermo (15 December 2004 – 31 December 2005)
Dr.ssa Giorgia Brancolini (15 April 2004 – 15 April 2007)

Dr.ssa Giovanna De Luca (1 July 2006 – 15 April 2007)

Dr. Toby Bell (1 january 2004-31 december 2006
Dr. Chris Finlayson (Post-doc) 1st Nov 2005-present
Fikri Alemdaroglu 04/2005-12/2006
Meryem Safak 01/2005-12/2006

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report of the Collaborative Research Project "SISAM"

Submission deadline: ***11 May 2007***

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (): 02-PE-SONS-023-SISAM Acronym / Short Title: SISAM Full Title: STRUCTURE ELUCIDATION OF SHEAR ORIENTED IONIC SELF-ASSEMBLED MATERIALS Project Leader name: Dr. CFJ Faul & Prof. Dr. Markus Antonietti Project Leader affiliation: University of Bristol / Max Planck Institute of Colloids and Interfaces Institutional home page (URL): www.bristol.ac.uk // www.mpikg-golm.mpg.de Project-related home page (URL): http://www.chm.bris.ac.uk/inorg/isa/sisamindex.html Reporting period: from 1 January 2006
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1:
Principal Investigator (name & affiliation): Prof. Dr. Gerrit ten Brinke, Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, The Netherlands. E-mail: G.ten.Brinke@rug.nl
Total Funding amount of the IP: ca. €195k
IP 2:
Principal Investigator (name & affiliation): Prof. Dr. Olli Ikkala

Molecular Materials Group Department of Engineering Physics and Mathematics Helsinki University of Technology P.O.Box 2200, FI-02015 TKK, Finland Email: Olli.Ikkala@tkk.fi
Total Funding amount of the IP: ca. €190k
IP 3:
Principal Investigator (name & affiliation): Dr. Charl FJ Faul Inorganic and Materials Chemistry School of Chemistry University of Bristol BS8 1TS, Bristol United Kingdom Email: charl.faul@bristol.ac.uk
Total Funding amount of the IP: ca. €200k

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

In this CRP a multidisciplinary approach was presented to investigate the macroscopic shear alignment of self-organised nanostructures: hydrogen-bonded and ionic-bonded polymer-amphiphile and oligoelectrolyte-amphiphile systems.

The synthesis of the compounds was mostly performed by MPIKG, while their alignment and characterization were carried out in RUG and HUT. In this way good collaboration between the CRP groups was established to discuss the general methodology, strategy and scientific results obtained, while each particular task of the project was performed at high scientific level within the three IP's.

General goals reached:

- Several model hydrogen and ionically bonded (ISA) supramolecular systems selected, synthesized and fully characterised.
- A new birefringence rheo-optical setup built and used, in conjunction with a specially modified tooth rheometer, to determine operating parameters for alignment of supramolecular materials.
- A new shear cell has been designed for use specifically with polyaniline-surfactant ISA systems.
- The production of a large variety of functional materials, notably the production of oligoaniline-surfactant complexes showing switchable functionality and synthesis and characterisation of pyrrole-containing surfactants.

The general conclusion reached was that induction of alignment could only be reached in certain of the model systems. In general, the presence of the ionic groups made the classical alignment strategies less applicable to these materials. Several strategies were employed to **investigate the broader scientific question** whether macroscopic alignment in such ionic systems was feasible in the following further studies.

Further studies:

In order to address the fundamental question of the feasibility of macroscopic alignment in ionically bonded supramolecular materials, the following investigations were performed on two model polymeric supramolecular systems. Both systems are similar

polymer-surfactant complexes, self-assembled on a nano-scale, that differ in the type of polymer-surfactant complexation. One system was a complex of poly(4-vinyl pyridine) ionically bonded with p-dodecyl benzene sulfonic acid (P4VP-DBSA), while the other was a hydrogen-bonded system of the same poly(4-vinyl pyridine) with 3-pentadecyl phenol (P4VP-PDP). As observed by SAXS, both systems reveal an essentially multi-domain lamellar morphology.

It was found that the ionic-bonded system is a more tough material compared to the hydrogen-bonded system and that the enhanced viscosity of the former is a limiting factor to achieve a high degree of alignment. On reducing the viscosity with temperature, the alignment of the ionic-bonded system noticeably increases, but here the decomposition temperature is another natural limit of the sample.

Small-angle X-ray scattering (SAXS) data suggest that the hydrogen-bonded systems can be quite well aligned both in *steady-state and oscillatory shear modes*. The orientational distribution of the lamellar normal is practically uniaxial and the orientation order parameter is ca. 0.8.

In the case of the ionic bonded systems, most reliable data were obtained under *steady-state shear*, when macroscopically uniform alignment was observed. The data obtained under large amplitude oscillatory shear (LAOS) were not fully reproducible. The degree of alignment of this sample is in general lower than for the hydrogen-bonded system. Besides, SAXS data reveal a significant biaxial distribution in the orientation of the lamellar normal. The latter, i.e., the biaxial distribution, is an interesting finding and appears to be a subject for further investigation in the near future.

Interesting results have also been obtained during the shear-induced alignment of supramolecular systems consisting of a polyisoprene-b-poly(2-vinylpyridine) diblock copolymers and octyl gallate (OG), where OG is hydrogen bonded to the vinylpyridine block of the PI-b-P2VP copolymer. It is found that the efficiency of the LAOS imposed to align the cylinder morphology samples is strongly influenced by the initial grain size of the structure. Freshly loaded samples, where the average size of the randomly oriented cylindrical domains is rather small, appear to be more suitable to achieve a high degree of alignment than pre-aligned samples where the initial grain size is increased.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

In general the project investigation was performed in accordance with the proposed work plan. The CRP has adhered very closely to the aims and goals, as set out on page 7 of the original Full Application. Further exciting new scientific goals have emerged from this collaborative research effort.

One objective that was implied throughout the original proposal was that macroscopic alignment of ISA systems would be achieved. However, high macroscopic alignment of the ionic-bonded systems investigated employing shear alignment strategies was not successful. In fact, the data obtained suggest a quite poor alignment compared to the hydrogen-bonded systems.

On the other hand, this finding was new, not expected, and a particular experimental challenge encountered during the investigative phase of the project, and it could not be predicted in advance. In this respect the investigation of the reasons for the difference in the alignment of ionic-bonded and hydrogen-bonded systems, as well as the determination of conditions and parameters to obtain uniformly aligned macroscopic samples, appear to be far-reaching scientific achievements of the CRP.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

- SONS Networking activity, involving several CRPs:
  "SONS Polymer, Amphiphiles and Nanostructured Materials" in Bristol/Bath, UK, held on June 12-15, 2007
- Possible involvement of CFJ Faul in collaborative work with the Eurodyna programme (meeting attended in Brussels, September 2006).
- One FP7 funding proposal submitted in a small collaborative project including O. Ikkala and CFJ Faul.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years):

- Developing strategies to reversibly address function (i.e. switchability) in supramolecular materials
- Possibly a call to provide funding for *feasibility studies* to take research from the lab into the commercial zone (i.e., not provide start-up money, but to help cover the area between laboratory research and start-up/spin-out company)

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme:

- Light administrative load.
- Interesting and relevant topics are explored.
- Scientific freedom
- European networking opportunities (workshops, conferences, symposia etc)

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures:

- The fact that different partner countries and their respective research bodies could not decide on a coherent funding strategy made finding suitable partners, and continuing with the second SONS round, extremely difficult.
- Difficulty in coordinating the starting times and availability of funding for all partners at the same time could be addressed in future calls.
- The fact that no feedback is allowed on referee comments during the application process for new funding (e.g. SONS II) makes this a non-transparent process, and probably needs revising or re-thinking.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

None

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

Publications:

E. Polushkin, S. Bondzic, A-J Schouten, O. Ikkala, G. ten Brinke "The influence of grain size on the alignment of hexagonally ordered cylinders of self-assembled diblock copolymer-based supramolecules", *Polymer*, **in press.**

R.A.H. Ras, M. Kemell, J. de Wit, M. Ritala, G. ten Brinke, M. Leskela, O. Ikkala, Hollow inorganic nanospheres and nanotubes with tunable wall thicknesses by atomic layer deposition on self-assembled polymeric templates, *Advanced Materials*, **19**(1), 102-106 (2007).

A. Laiho and O. Ikkala, A rheo-optical apparatus for real time kinetic studies on shear-induced alignment of self-assembled soft matter with small sample volumes, *Reviews of Scientific Instruments*, **78**, 015109 (2007).

D. Franke, M. Vos, M. Antonietti, N. A. J. M. Sommerdijk and C. F. J. Faul, 'Induced Supramolecular Chirality in Nanostructured Materials: Ionic Self-Assembly of Perylene-chiral surfactant complexes', *Chem. Mater.*, **2006**, *18*, 1839-1847.

C. F. J. Faul, 'Liquid-Crystalline Materials by the Ionic Self-Assembly Route', *Mol. Cryst. Liq. Cryst.* **2006**, *450*, 55-65

D. Franke, C. C. Egger, B. Smarsly, C. F. J. Faul and G. J. T. Tiddy, 'Synthesis and Phase Characterization of a Double-tailed Pyrrole-containing Surfactant: A novel tecton for the production of functional nanostructured materials', *Langmuir*, **2005**, *21*, 2704-2712.

In-situ SAXS study on the alignment of ordered systems of comb-shaped supramolecules: A shear-induced cylinder-to-cylinder transition, E. Polushkin, S. Bondzic, J. de Wit, G. Alberda van Ekenstein, I. Dolbnya, W. Bras, O. Ikkala and G ten Brinke, *Macromolecules*, **38**(5), 1804-1813 (2005).

Self-Assembly and Electrical Conductivity Transitions in Conjugated Oligoaniline/Surfactant Complexes, Z. Wei, T. Laitinen, B. Smarsly, O. Ikkala, C.F.J.

Faul, *Angewandte Chemie Int. Ed.,*, **44**(5), 751-756 (2005).

E. Polushkin, S. Bondzic, J. de Wit, G. Alberda van Ekenstein, I. Dolbnya, W. Bras, O. Ikkala, G. ten Brinke."In-situ SAXS study on the alignment of ordered systems of comb-shaped supramolecules: A shear-induced cylinder-to-cylinder transition", *Macromolecules*, **2005**, 38, 1804-1813.

"Nanorod Engineering by Reinforcing Hexagonally Self-Assembled PS-b-P4VP(DDP) with PPE" W. van Zoelen, G. Alberda van Ekenstein, E. Polushkin, O. Ikkala and G. ten Brinke, Soft Matter, 2005, 1, 280-283.

E. Polushkin, S. Bondzic, A-J Schouten, O. Ikkala, G. ten Brinke "Detailed SAXS study on the order-to-order transition from lamellar to cylindrical structure of comb-shaped supramolecules system", **in preparation**.

E. Polushkin, A. Laiho, O. Ikkala, C.F.J Faul, G. ten Brinke "Shear alignment of ionic-bonded polymeric complexes as observed by SAXS", **in preparation**.

Conferences: See below

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

None

1 D. Patents and industry collaborations

None

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

1 F. Participation in other conferences

Only the most relevant are listed below:

Evgeny Polushkin Shear alignment of ionic-bonded polymeric complexes as seen by SAXS" **Oral presentation** at SONS conference 2006, June 29 –July 1 2006, Pisa, Italy.

Charl FJ Faul, "Strategies for the alignment of supramolecular materials" **Oral presentation** at SONS conference 2006, June 29 –July 1 2006, Pisa, Italy

Olli Ikkala: **Invited talk** "Functional Polymeric Materials Based on Hierarchical Self-Assembly" at 4th International Symposium on High-Tech Polymer Materials (HTPM-IV), in Fragrant Hill, Beijing, China, on May 14-20, 2006.

R.H.A Ras, M. Kemell, J. de Wit, M. Ritala, G. ten Brinke, M. Leskelä, O. Ikkala, Hollow inorganic nano-objects fabricated by atomic layer deposition on self-assembled polymeric templates, **oral presentation** at the 40th annual conference of the Finnish Physical Society, 9-11 March 2006, Tampere, Finland

Olli Ikkala: **Invited talk** "Hierarchical Self-Assembly of Polymeric Complexes: A Concept for Functional Materials", at Pacifichem 2005, Honolulu, Hawaii, December 15 - 20, 2005.

Evgeny Polushkin: In-situ SAXS study of the ordered systems of comb-shaped supramolecules: alignment and collapse. **Oral presentation** at the 5th International Symposium "Macromolecular Mobility and order in Polymer Systems", 20-24 June 2005, Saint Petersburg, Russia.

Gerrit ten Brinke: New insights in comb-shaped supramolecules based nanomaterials. **Oral presentation** at the European Polymer Congress EPF-2005, June 27 – July 1, 2005, Moscow, Russia.

D. Franke, M. Antonietti, C.F.J. Faul, Towards Novel Functional Materials via the ISA Route, **Poster presentation** at MC7 - Functional Materials for the 21st Century (University of Edinburgh, Scotland, U.K.), 5 – 8 July 2005

C.F.J. Faul, Switchable functional nanostructured materials by Ionic Self-Assembly, **Oral presentation** at MC7 - Functional Materials for the 21st Century (University of Edinburgh, Scotland, U.K.), 5 – 8 July 2005

Olli Ikkala: Hierarchical Self-Assembly of Polymeric Complexes: a Concept for Functional Materials, **invited talk** at ERA-Chemistry Workshop - "Hierarchically Organised Chemical Structures: from Supramolecularity to Hybrid Materials", Max Planck Institute for Polymer Research, Mainz, Germany, February 16-19, 2005.

C.F.J. Faul, Switchability, Biological Materials and Ionic Self-Assembly: New Routes towards Self-Assembled Biodevices?, **Oral presentation** at EMRS Spring Meeting, Strasbourg, France, June 2005

Ari Laiho, Sini Kivi, Olli Ikkala, Characterization of shear induced nanostructures by rheo-optic means, **Poster presentation** at the 39th annual conference of the Finnish Physical Society, 17-19 March 2005, Espoo, Finland

Ari Laiho, In-situ rheo-optical studies on shear-aligned complex fluids, **Oral presentation** at the 2nd Scandinavian Workshop on Scattering from Soft Matter, 3-4 February 2005, Lyngby, Denmark.

Evgeny Polushkin: Shear-Induced Collapse of Hexagonal Phase" **Poster presentation**

at the European Polymer Congress EPF-2005, June 27 – July 1, 2005, Moscow, Russia.

Olli Ikkala: Hierarchical Self-Assembly of Polymeric Complexes: A Concept for Functional Behaviour, **invited talk** at COST D-31 meeting "Non-Covalent Chemical Systems with Selected Functions", Prague, November, 4–7, 2004

Olli Ikkala: Hierarchical Self-Assembly of Polymeric Complexes: A Concept for Functional Materials, **invited talk** at 40th IUPAC Symposium on Macromolecules, July 4-9, 2004, Paris, France.

Evgeny Polushkin: In-situ SAXS study on the alignment of ordered systems of comb-shaped supramolecules, **Oral Presentation** at Interfaces and Colloidal Systems, Structure and Dynamics of Polymers and Colloidal Systems Euresco Conference, 10-15 September 2004, Giens, France

Olli Ikkala: Hierarchical Self-Assembly of Polymeric Complexes: A Concept for Functional Behaviour, **invited talk** at "Interfaces and Colloidal Systems" (An ESF/Euresco Meeting), September 10-15, 2004, Giens, France.

Olli Ikkala: Self-organization of polymeric comb-shaped supramolecules: Tailored properties and functions, **invited talk** at "Nanopatterns and Nanostructures at the Interfaces", Mulhouse, France, 12-15 October 2003.

Appendix 2. Scientific & technical personnel involved in the CRP
Personnel directly funded by the EUROCORES Programme Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD
RUG: September 2003 – September 2006 Dr. Evgeny Polushkin
HUT: 2003 Dr. Nicole Volk - 1.9.-31.12.2003 2004 Dr. Nicole Volk - 1.1.-31.7.2004 Dr. Robin Ras - 1.8.-31.12.2004 2005 Dr. Robin Ras - 1.1.-31.12.2005 2006 Dr. Robin Ras - 1.1-30.9.2006
MPIKG: September 2003 – February 2006 Dr. Danielle Franke

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (): Acronym / Short Title: *(NANO-SMAP)* Full Title: *Nanochemical patterning combining selective molecular assembly systems and colloidal lithography* Project Leader name: *Marcus Textor* Project Leader affiliation: *ETH Zurich (ETHZ)* Institutional home page (URL): *www.ethz.ch* Project-related home page (URL): www.smap.ethz.ch Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1 ETH Zurich (ETHZ)
Principal Investigator (name & affiliation): Prof. Marcus Textor, ETH Zurich
Total Funding amount of the IP: **CHF 270,511**
IP 2 Chalmers University of Technology (CUT)
Principal Investigator (name & affiliation): Prof. Bengt Kasemo
Total Funding amount of the IP: **SEK 1,500,000**
IP 3 Utrecht University (UU)
Principal Investigator (name & affiliation): Prof. Alfons van Blaaderen
Total Funding amount of the IP: **€ 192,000**
IP 4 Dresden University of Technology (DUT)
Principal Investigator (name & affiliation): Prof. Hans-Jürgen Adler
Total Funding amount of the IP: **€ 135,000**

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

A. Colloidal assembly as mask for subsequent etching/lithography (ETH, CUT, UU)
Self-organized, densely packed monolayers of monodisperse latex particles (micron- and submicron-sized) were successfully produced across large areas and etched under optimized reactive plasma conditions to shrink the size of the particles while preserving at the same time the order of the assembled particles. Such nanodot arrays were used as mask translating the particle array into chemical patterns composed of the underlying SiO_2/TiO_2 chemistry. Assemblies of charged colloids at controlled average spacings were produced and used to generate nanopatterns of gold in a silicon oxide background for further modification using alkanethiol chemistry (colloidal lithography). The ability to pattern structures with colloids of too strong scattering strength (such as ZnS or TiO_2) for applications such as colloidal lithography by use of optical tweezers was realized in the first SONS period. The technique was now successfully extended to so-called counterpropagating optical tweezers. This allows for production of extended patterns of multiple particles in time-shared traps as well as the ability to manipulate strongly scattering anisotropic objects like rodlike particles. First tests with an automated version of our optical tweezers set up that allows trapping of new particles using an accurate x-y-z piezo stage and an image processing step to have accurately absolute position control showed increased accuracy.

B. Pattern stability (ETHZ, Ian Wark Research Institute, Univ. of South Australia)
To improve the long-term stability of background passivation (an important issue for the study of cell-surface interaction), a novel technique for the covalent immobilization of PEG-graft polyelectrolytes was successfully developed, based on a combination of aldehyde-plasma functionalisation of the substrate and spontaneous assembly of the functional polymer.

C. Synthesis of novel oligo(EG)-functionalized alkane phosphates for SAMs (DUT)
A series of novel, terminally functionalised oligo(ethylene glycol)-substituted alkane phosphates and –phosphonates were successfully synthesized and tested for their ability to form self-assembled monolayers (SAMs) on TiO_2 and Al_2O_3 substrates. The SAMs were characterized with respect to assembly behaviour, order, and stability. Availability of theses molecules opens up new ways of producing biologically meaningful patterns in the context of the SMAP process (protein-resistant SAMs on TiO2; proteins specifically immobilized on functionalized PLL-g-PEG adlayers on SiO2 through biotin-streptavidin or NTA-Ni^{2+}-histag coupling).
Additionally, hyperbranched polyglycidol (M_W= 2500 g/mol) was functionalized with (alkyl)phosphat- as well as (alkyl)phosphonate groups and investigated for its self-assembly kinetics, stability and surface properties. The interaction of such layers with single protein solutions and serum protein impact is currently under investigation.

D. Protein nanopatterns (CUT, ETHZ)
Large areas characterized by regular patterns of TiO_2 pillars in a SiO_2 background were successfully produced via the "plasma-shrinked colloidal pattern" masks. After the lift-off process the oxide contrast was translated into a protein nanopattern using the SMAP process. Using the gold nanopatterns in a SiO2 background produced by colloidal lithography, cell-adhesive proteins

were patterned and characterized by a combination of QCM/SPR and AFM. Protein patches with ~ 40 laminin proteins per patch were created and their ability to bind antibodies studied. Interestingly, laminin bound at nanostructures smaller than the characteristic size of the protein showed higher antibody-binding efficiency compared to laminin bound at homogenous/macroscopic surfaces. Collaborative cell studies with laminin-nanopatterned surfaces demonstrated that the nanoscale patches affect cell-surface binding mechanism and are able to prevent the formation of focal adhesions.

E. Nanocavities for Protein Interactions Studies (ETHZ, CONFIDENTIAL/planned patent application)

The etched particle patterns were further used as a template for the creation of nanocavity arrays using replica molding. The surface of the PDMS replica was PEGylated and the cavities were filled with fluorescently labeled protein in solution. The presence of proteins was detectable by light microscopy to the single protein level. This will become a powerful tool to investigate protein-protein interactions in very small volumes of liquid confined in the nanocavities.

F. Wet Particle Lithography (ETHZ, CUT)

We have developed a method to assemble micron sized particles in a microfluidic device from particle suspensions and to use the created particle arrays as a protecting mask for the creation of ordered protein patterns. Particles were therefore introduced into the microfluidic channels and guided to assemble at an engineered barrier. The created ordered particles patterns were then used as a mask to produce protein patterns in the channels totally in liquid as follows: First PLL-*g*-PEG was adsorbed everywhere but at the touching points between the particles and the surface. Changing the PLL-*g*-PEG adsorption times produced different sizes of PLL-*g*-PEG free areas underneath the particles. The particles were subsequently removed from the channels and proteins were immersed to adsorb to the PLL-*g*-PEG free areas.

G. Photolithographic patterning on polymeric substrates to create protein patterns (ETHZ)

Direct patterning of polymeric substrates using photolithography was developed. Using regular photoresists to structure Si-wafers was not suitable due to the aggressive organic solvents present in the resists. In collaboration with YMC Switzerland we have developed a resist that is compatible with polymeric substrates such as polystyrene and PDMS. The resist patterns on these substrates were then transferred into a PEG-protein or a protein-protein contrast using a modified Molecular Assembly by Lift-off (MAPL) approach (Falconnet et al., Adv. Funct. Mater., 2004).

H. Colloidal nanopatterns to study rupture of phospholipids vesicles (CUT)

Colloidal nanopatterning was used to create arrays of nanocavities in silicon oxide surfaces or gold/silicon dioxide surfaces. Phospholipid single unilaminar vesicles were ruptured at these interfaces and the influence of the nanoscale structures studied by quartz crystal microbalance and atomic force microscopy and compared to Monte Carlo simulations. Enhanced rupture was seen for nanostructured surfaces and changes in the fluidity of the bilayer.

I. General Activities

SONS Executive group (2005-2006, Chair: M. Textor): Organisation of scientific program for SONS Annual Meeting 2006, Pisa, I.

The scientific results presented above would clearly not have been achieved without the existence of the ESF SONS program and the corresponding concerted funding of the four partners by the national funding agencies.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

ETHZ: The production of patterns in the size range below 200 nm based on TiO2/SiO2 prepatterns were not further followed as the combined approach between CUT and ETHZ proofed to be the more straightforward, and at the end fully successful approach (see H. Agheli, J. Malmström, E. M. Larsson, M. Textor and D.S. Sutherland, Nanoletters 6(6): 1165-1171 (2006)).

UU: Placement of colloidal particles with optical tweezers in a completely automated way. We are still actively pursuing this approach as originally planned, it turned out to be too ambitious to achieve in the allotted time.

DUT: The synthesized SAM molecules based on functionalised oligo(ethylene glycol)-substituted alkane phosphates and –phosphonates were only investigated on unstructured (homogesous) metal oxide substrates until now. The adhesion behavior and interaction of such layers on structured/patterned TiO_2/SiO_2 substrates in contact with single protein solutions and serum proteins is currently under investigation and will be finished by end of 2007.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

ETHZ and CUT

The enabling technology of nanopatterning over large areas and with large pattern-to-pattern distances – based on colloidal lithography and selective etching has become an important aspect in two EU FP7-NMP-SMALL proposals submitted May 4, 2007 (Coordinator: B. Kasemo and M. Textor resp.). Moreover, this technology is now used extensively in a running project of the Swiss Competence Centre for Materials Science and Technology (CCMX) on liposomes and lipidic membranes supported by nanostructured substrates for biosensing.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

An area that has evolved in the last few years (partly in projects of the SONS I program) and is believed to have great promise for the future is the assembly of hybrid and chimera materials into well-defined three-dimensional structures and materials with outstanding properties (mechanical, biochemical, responsive, bioactive). This could be a potential topic carrying elements of the SONS I and II program, but with a stronger focus towards the generation of useful materials and their applications. The incorporation of biological building blocks such as peptides and oligonucleotides – that steer the organization into well defined supramolecular structures – into synthetic organic polymers and their combination with inorganic materials opens up a very promising and wide field of efficient production of novel materials, taking advantage of both biological design rules and synthetic materials properties.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

The EUROCORES/SONS proved for our CRP team to be an ideal platform to start transdisciplinary research with partners working in different, complementary fields, both within our SONS project as well as with further partners within the SONS program. Very fruitful in this

respect are the SONS workshops with selected topics relevant to several SONS projects. Overall, it was very worth the effort to go through the time-consuming process related to the national funding schemes of SONS. Also, the SONS Annual Meeting in 2006 was considered to be a very successful scientific meeting and a great opportunity to get an overview over the many different aspects and application of self-organized nanostructures.

Moreover, the timing of SONS I was ideal in terms of the opportunity to continue research and established partnership in the context of the EU FP7 Programme

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The main disadvantage is considered to be the "instability" of national participation in the ESF Research Programmes. The decision of some of the countries to discontinue participation in the SONS II Programme has been the main reason why it did not make sense for our consortium to submit a continuation project in SONS II.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

"*Wet Particle Lithography"*, T.M. Blättler, E. Thomasson, M. Röllinghoff, J. Vörös, M. Textor and E. Reimhult, to be submitted to Nano Letters (2007)

M. Gnauck, E. Jähne, Th. Blättler, S. Tosatti, M. Textor, H.-J. Adler, "*Carboxy-Terminated Oligo(ethylene glycol)-Alkane Phosphate: Synthesis and Self-Assembly on Titanium Oxide Surfaces"*, Langmuir 23(2): 377-381 (2007)

"Large Area Protein Nanopatterning for Biological Applications", H. Agheli, J. Malmström, E. M. Larsson, M. Textor and D.S. Sutherland, Nanoletters 6(6): 1165-1171 (2006)

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

ETHZ

T.M. Blättler, P. Muff, M. Ochsner, M. Textor and J. Vörös, *"High Fidelity Photolithographic Protein Patterning on Polymeric Substrates"*, to be submitted to Biomaterials (2007)

B. Städler, T.M. Blättler, N. Graf, J. Vörös, A. Franco-Obregon, *"Real-Time Examination of Cell Fusion Using AFM"*, to be submitted to FEBS (2007)

T.M. Blättler, A. Binkert, M. Zimmermann, M. Textor, J. Vörös and E. Reimhult, *"From particle self-assembly to functionalized sub-micron protein patterns"*, to be submitted to Nanotechnology (2007)

J.W. Lussi, D. Falconnet, J.A. Hubbell, M. Textor G. Csucs, *"Pattern stability under cell culture conditions"*, Biomaterials 27(12): 2534-2541 (2006)

T. Blaettler, C. Huwiler, M. Ochsner, B. Staedler, J. Voeroes and M. Grandin, *"Nanopatterns with Biological Functions"*, J Nanoscience and Nanotechnology 5(3): 215-219 (2006)

T.M. Blättler, S. Pasche, M. Textor and H.J. Griesser, *"High Salt Stability and Protein Resistance of Poly(L-Lysine)-g-Poly(Ethylene Glycol) Copolymers Covalently Immobilized via Aldehyde Plasma Polymer Interlayers on Inorganic and Polymeric Substrates*", Langmuir 22 (13): 5760-5769 (2006)

C. Huwiler, M. Halter, K. Rezwan, D. Falconnet, M. Textor, J. Vörös, *"Self-assembly of Functionalized Spherical Nanoparticles on Chemically Patterned Microstructures*", Nanotechnology 16(12): 3045-3052 (2005)

J.W. Lussi, C. Tang, P.-A. Kuenzi, U. Staufer, G. Csucs, J. Vörös, G. Danuser, J.A. Hubbell, M. Textor, *"Selective Molecular Assembly Patterning at the Nanoscale: A Novel Platform to Produce Protein Patterns by e-beam Lithography of Indium-Tin-Oxide/Silicon Oxide Coated Glass Substrates"*, Nanotechnology 16:1781-1786 (2005)

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

CUT

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

C.C. Berry, A.C.G Curtis, R.O.C. Oreffo, H. Agheli and D.S. Sutherland "*Human fibroblast and human bone marrow cell response to lithographically nanopatterned adhesive domains on protein rejecting substrates*" accepted for publication in IEEE Transactions of Nanobioscience

K. Dmitrievski and B. Kasemo "*MonteCarlo simulations of the vesicles of different charges with a silica"* Manuscript for submission to Journal of Physical Chemistry

B. Seantier, I. Pfieffer, K. Dimitrievski, S. Petronis, D.S.Sutherland and B. Kasemo "*Formation of phospholipid bilayers on topographically nanostructured surfaces*", Manuscipt ready for submission to Langmuir.

UU

M. E. Leunissen, C. G. Christova, A.-P. Hynninen, C. P. Royall, A. I. Campbell, A. Imhof, M. Dijkstra, R. van Roij, and A. van Blaaderen *Ionic colloidal crystals of oppositely charged particles*, *Nature* **437**, 235-240 (2005).

A. van der Horst, A. I. Campbell, L. K. van Vugt, D. A. M. Vanmaekelbergh, M. Dogterom, A. van Blaaderen, *Manipulating Metal-Oxide Nanowires using Counter-Propagating Optical Line Tweezers*, submitted 2007 to Optics Express.
A. I. Campbell, et al., *Monodisperse high index rutile and anatase titania colloids*, in preparation.

DUT

Loppacher, C.; Zerweck, U.; Koehler, D.; Rodenstein, M.; Jähne, E.; Luther, R.; Adler, H.-J.; Eng, L.M.: "*Physical vapour deposition of alkyl phosphonic acis on mica and HOPG investigated by NC-AFM"*, Nanotechnology 18 (2007) 084003

Britze, A.; Moosmann, K.; Jähne, E.; Adler, H.-J.; Kuckling, D.: *"Synthesis of Block Copolymers Modified with Phosphonate Ester Groups Using Nitroxide-Mediated Radical Polymerisation*", Macromol. Rapid Commun. 2006, 27, 1906-1912

Lukaszcyk, J.; Smiga, M.; Jaszcz, K.; Adler, H.-J.; Jähne, E.; Kaczmarek, M.: *"Evaluation of Oligo(ethylene glycol) Dimethacrylates Effects on the Properties of New Biodegradable Bone Cement Compositions"*, Macromol. Biosci. 2005, 5, 64-69.

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Science City Information Days at ETH Zurich for the general public: Lecture on Surfaces, Nanotechnology, Biomedical Applications and Collaboration in the European Framework (April 2007).

1 D. Patents and industry collaborations

Industrial collaboration

Collaboration established with YMC Switzerland. In a joint project YMC Switzerland has developed a suitable photoresist to be used on polymeric substrates. We developed the process to produce protein patterns on polystyrene and PDMS (ETHZ)

Collaboration with company Leister Technologies, Switzerland, established in the context of using colloidal lithography for producing nanopores and surface-supported lipidic bilayers containing transmembrane proteins for application as drug screening platform (EU FP7-NMP-SMALL proposal submitted May 4, 2007 (ETHZ, PI: M. Textor)

Patents (planned – confidential)

Nanocavities for bulk-solution protein-protein interactions using negligible amounts of solution

(ETHZ)

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

Exchange of PhD students/postdocs between institutions of CRP:

Diploma thesis of Elsa Thomasson (CUT) carried out at ETHZ (working on Wet Particle Lithography, total of 8 month)

Research stay of Mandy Gnauck (TUD) and Rene Luther (TUD) at ETHZ in September 2005 and in May 2007 (total of 6 weeks)

Research stay of Evelin Jähne (senior scientist, TUD) at ETHZ in May 2007 (2 weeks)

1 F. Participation in other conferences

Please list only the most relevant

ETHZ

NSTI Nanotech 2007, Convention Center, Santa Clara, USA, May 2007 (T.M. Blättler and E. Reimhult, contributed talks)

ESF SONS Conference 2006, Hotel Granduca, Pisa, Italy, June 29 – July 1, 2006 (T.M. Blättler and E. Reimhult, contributed talks)

"Design of Biointerfaces at the Micro- and Nanoscale and Application to Implants and Cell Culture Substrates with Controlled Microenvironments", NanoBio Integration Conference, Tokyo, Japan, December 2006 (M. Textor, keynote speaker)

"Challenges in the Modification and Characterization of Two- and Three-Dimensional Biointerfaces", 53rd AVS International Symposium, San Francisco, USA, November 2006 (M. Textor, invited)

"Modification of biointerfaces to control the interactiveness with proteins and cells", ECOSS, Paris, France, September 2006 (M. Textor, invited)

„Design of Biointerfaces: from two-dimensional surfaces to three-dimensional substrates", 2nd International Symposium „Interface Biology of Implants", Rostock, Germany, May 2006 (M. Textor, keynote)

ESF Conference "Biological Surfaces & Interfaces", San Feliu de Guixols, Spain, June 2005 (J. Vörös, invited talk; T. Blättler, poster, M. Grandin, poster);

SONS workshop on "Surface Nanopatterning", Tirrenia, Italy, June/July 2005 (J. Vörös, invited talk; T. Blättler, poster);

BioNanotechnology 3, Sussex University, Brighton, UK, September 2005 (T. Blättler, contributed talk);

Australasian Polymer Conference, Adelaide, Australia, March 2005 (M. Textor, invited talk)

Summer School on Biointerface Engineering Italy, Ispra, Italy, November 2005 (M. Textor, invited talk)

CUT

West Sweden Business forum 8th Sept 2004 (D.S. Sutherland, invited talk)

South Korea-Sweden Joint Symposium Daejon South Korea 16th-20th October 2004 (D. S. Sutherland, invited talk)

First International Symposium on Biointerfacial Science, Duke University South Carolina USA May 12-14th 2005 (D. S. Sutherland invited talk)

EMRS, Strasbourg, May 31st-June 3rd 2005 (D. S. Sutherland invited talk)

Germany-Sweden Joint Symposium, Rostock Germany, November 22nd -23rd, 2005
(D. S. Sutherland invited talk)

UU

A.I. Campbell, A. van der Horst, L.K. van Vugt, A. van Blaaderen, *Surface Patterning with ZnO*

Nanowires, SONS progress meeting, Dresden, Germany, 26-05 Mei 2005, oral.
M. Leunissen, A.P. Hynninen, C. Christova, C.P. Royall, A. Campbell, A. Imhof, M. Dijkstra, R. van Roij, A. van Blaaderen, *'Ionic' crystals of oppositely charged colloids,* Department Day, Utrecht, The Netherlands. 22 June 2005, oral, contributed.
E.C.M. Vermolen, E.C.M., A.I. Campbell, D.L.J. Vossen, A. van der Horst, A. van Blaaderen, *Creating templates and manipulating photonic crystals using optical tweezers,* Photon Physics, Amsterdam, The Netherlands. 28 June 2005, poster.
A.I. Campbell, A. van Blaaderen, *Nanopatterning of Surfaces using Self-Organized and Optical Tweezer Techniques,* SONS Network Workshop on Surface Nanopatterning, Pisa, Italy. 30 June - 01 July 2005, oral.
A.I. Campbell, E.C.M. Vermolen, A. van der Horst, D.L.J. Vossen, A. van Blaaderen, *Creating templates and manipulating photonic crystals using optical tweezers,* Liquid Matter Conference, Utrecht, The Netherlands. 2-6 July 2005, poster.
C. Christova, M. Leunissen, A.P. Hynninen, P. Royall, A. Campbell, A. Imhof, M. Dijkstra, R. van Roij, A. van Blaaderen, *Ionic colloidal crystals of oppositely charged particles,* 6-th Liquid Matter Conference, Utrecht, The Netherlands. 02-04 July 2005, oral.
D.C. 't Hart, J.H.J. Thijssen, M. van der Maas, A. van der Horst, A. Campbell, C. Graf, A. van Blaaderen, *Analysis and Control over Defects in Photonic Crystals,* Three-Dimensional Multifunctional Ceramic Composites Workshop, Urbana Champaign, USA. 03 Oktober 2005, oral.
M. Leunissen, C. Christova, A.P. Hynninen, P. Royall, A. Campbell, A. Imhof, M. Dijkstra, R. van Roij, A. van Blaaderen, *Ionic colloidal crystals of oppositely charged particles,* Soft Matter Days 2005, Bonn, Germany. 01-04 November 2005, oral.
A.I. Campbell, E.C Vermolen, A. van der Horst, D.L.J. Vossen, A. van Blaaderen, *Creating templates and manipulating photonic crystals.*M. *using optical tweezers,* Soft Matter Days, Bonn, Germany. 1-4 November 2005, Poster.
A.I. Campbell, A. van der Horst, J. Schütz-Widoniak, A. van Blaaderen, *Titania Colloids: Synthesis, Patterning and Crystal Doping,* SONS progress meeting, Goteborg, Sweden, 09 November 2005, oral.
D.C. 't Hart, J.H.J. Thijssen, A. van der Horst, A. Campbell, A. Imhof, A. van Blaaderen, *Analysis and Control over Defects in Photonic Colloidal Crystals,* NanoNed Symposium, Groningen, The Netherlands. 08-09 December 2005, oral.
E.C.M. Vermolen, A.I. Campbell, M.E. Leunissen, D.l.J. Vossen, A. van der Horst, A. van Blaaderen, *Creating templates for nucleation and growth of colloidal (photonic) crystals,* NanoNed/MicroNed Symposium, Groningen, The Netherlands. 8-9 December 2005, Poster.
M. Leunissen, C. Christova, A.P. Hynninen, P. Royall, A. Campbell, A. Imhof, M. Dijkstra, R. van Roij, A. van Blaaderen, *Ionic colloidal crystals of oppositely charged particles,* FOM-Decemberdagen 2005, Veldhoven, Nederland 13-14 December 2005, oral.
E.C.M. Vermolen, A.I. Campbell, M.E. Leunissen, D.L.J. Vossen, A. van der Horst, A. van Blaaderen, *Creating templates for nucleation and growth of colloidal (photonic) crystals,* FOM-decemberdagen, Veldhoven, The Netherlands. 13-14 December 2005, Poster.
A.I. Campbell, A. van der Horst, A. van Blaaderen, *Introducing Defects into Colloidal Photonic Crystals Using Optical Tweezers,* FOM December Dagen, Veldhoven, Netherlands. 13-14 December 2005, poster.

DUT

Workshop Karpcz 2007 (DUT and Silesian University of Technology) E. Jähne, contributed talk

Polymers and Coatings 2006; GDCh-Conference, 24.-26. September 2006 in Mainz; Mandy Gnauck, poster,

SONS-Conference 2006, Self organised nano-structures (SONS); 28.06.-1.07.2006 in Pisa, E. Jähne, contributed talk, Mandy Gnauck, poster, Rene Luther, poster

7. IPF-Kolloquium 'Innovative Coating Materials and -technologies', 8. - 9. November 2006 in Dresden, Mandy Gnauck, poster

API conference 2006, Mainz, M. Gnauck, poster, R. Luther, poster.

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

ETH Zurich (ETHZ)
Heather Michelle Grandin, ETH Zurich, Postdoc, from 01.2004 to 05.2006
Thomas Blättler, ETH Zurich, PhD student, from 01.04.2004 to 30.09.2007 (PhD defence planned for September 2007)

Dresden (DUT)
Mandy Gnauck, TU Dresden, PhD student, from 1.10.2004 to 31.12.2007
Rene Luther, TU Dresden, PhD student, from 1.1.2006 to 31. 12. 2007

Chalmers (CUT)
Hossein Agheli 01.01.2004 to 31.04.2006 (57% of PhD position)
Duncan Sutherland 01.01.2004 to 31.12.2005 (25% of senior postdoc position)

Utrecht (UU)
Andrew Campbell 01-04-2004 to 01-10-2006 (postdoc position)

EUROPEAN SCIENCE FOUNDATION

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
SPANAS

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (): Acronym / Short Title: SPANAS *Full Title: System for Photonic Adjustment of Nano-scale Aggregated Structures* Project Leader name: *Dag Hanstorp* Project Leader affiliation: *Göteborg University, Sweden* Institutional home page (URL): *www.physics.gu.se* Project-related home page (URL):- Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Prof. Dag Hanstorp, Göteborg University, Sweden
Total Funding amount of the IP *SEK 2 Million (appr. EUR 210 000)*
IP 2
Prof. Dr. Stefan Sinzinger, TU-Ilmenau, Germany
Total Funding amount of the IP *appr. EUR 214 000*
IP 3
Prof. Jesper Glückstad, Risø National Laboratory (RNL), (now merged with Technical Univ. of Denmark)
Total Funding amount of the IP *DKK 1.744.056 (appr. EUR 210 000)*
IP 4

Dr. Gordon Love, Durham University, UK.
Total Funding amount of the IP *GBP386,612 (Approx 568K Euros)*

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

Note: Our programme runs for 4 years, so there is more than half a year left to run at the time of writing.

The general theme of the SPANAS collaboration has been to develop new optical tools that can be used to manipulate large ensembles of particles. The long term goal has been to design user friendly automated systems where a large variety of experiments can be conducted. Several types of experimental platforms have been developed, where a major effort has been directed towards the construction of optical systems that can be used to manipulate particles in microfluidic systems. These systems are developed to be used in the field of micro biology where experiments on single cells in controlled environments can be conducted. The work has been made possible by the combined expertise of the four participating groups. In the field of optics we have developed methods for optical manipulation using liquid crystals, planar optics as well as the General Phase Contrast method (GPC). New opportunities and ideas have meant that also other exciting results and publications were produced. More specifically, we achieve the following:

1. We have demonstrated full 3D control of optical tweezers using a transmissive liquid crystal prism/lens. This has the advantages of simplicity/high efficiency over conventional (holographic) techniques. Furthermore, we used this technique to demonstrate an oscillating optical double potential well, or “optical juggling” (Hands *et al.* 2006).

2. We have performed a number of experiments on particles in counter-propagating beams. Instead of being pushed together in the centre, the particles form stable arrays via a mechanism called “optical binding”.

3. We have combined liquid crystal correction and control elements with a planar optical system to produce a compact dynamical microoptical system (Amberg *et al.* 2007).

4. We have developed a microfluidic systems in which trapped objects can be moved between different media. Lithographic methods in combination with moulding in rubber silicon (PDMS) allowed us to produce an arbitrary microfluidic system. Objects can be moved around the fluidic system using optical tweezers at the same time as they are observed with advanced microscopic techniques. A sharp gradient between two media can be produced in this system. This allow us to move cells between different

environments on a time scale of 100 ms. This is a major improvement as compared with other microfluidic systems where the cell is moved by the media itself.

5. The above mentioned system has been used in experiments in collaboration with biologists. First, we have investigated the oxygenation cycle in red blood cells. The cells were placed in a microfluidic system where they were expose the water of alternating high or low concentration of free oxygen, and the up-take or release of the oxygen is monitored by applying Raman spectroscopy. Second, we have made extensive studies of yeast cells, where we have studied volume changes of the cells as they were exposed to media of different salt concentrations. The volume changes, caused by the osmotic process, were monitored using a video camera and an image analysis program.

6. We have developed a system where we integrate micro optical structures into the channel walls of a micro fluidic system. The properties of PDMS meant that it was an ideal material for integration into micro fluidic channels and replication of sub micrometer diffractive optical elements. Thus we can use the material for the integration of the replicated micro optical elements in a sandwich set-up in the optical tweezers for parallel 3D-manipulation of micro particles in different diffractive orders. In the experiment we worked with a binary (two phase levels) grating. However, the replication of diffractive elements up to eight phase levels for improved efficiency has been demonstrated. The sandwich configuration is necessary in order to avoid index matching of the grating by either the liquid in the channel or the immersion oil.

7. We have developed a stand-alone biophotonics workstation, based on the General Phase Contrast method. This is currently being tested by external partners with micro-biological expertise. This function as a precursor for a commercial launch in the near future. The system can produce more than 100 simultanous laser traps supporting multiple wavelengths. It is a true real-time, fully computerized interactive or vision-guided system with 3D observation and manipulation capabilities. It requires no immersion liquid, and the working distance of up to 1 cm allows side viewing. In the future it will be possible to extend the system for spectroscopic observations.

8. We discovered a new effect in liquid crystals, whereby particles dispersed in a nematic liquid crystal cell are attracted towards an isotropic region generated by local laser heating. This was explained in terms of a gradient in the order parameter and the flexoelectric effect ((Tatarkova *et al.* 2007).

9. We used wavefront sensing techniques from adaptive optics to measure the orbital angular momentum of beams with helical wavefronts. Our technique unambiguously measured the sign as well as the magnitude of the wavefronts (Leach *et al.* 2006).

10. We developed a “smart camera” – based on our adaptive optics control systems – which can monitor the position of a number of particles at high speed and continuously. The system has been used to track the Brownian motion of arrays of particles held in optical tweezers.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

The original research plan presented in the SPANAS proposal was written in 2002, and our research has been carried out within the general framework of research suggested in the proposal. It is obvious, however, that we during this five years period have found new interesting research ideas that were not in the original proposal. However, we find that this is exactly the way a successful research program should be conducted. We have encountered many scientific problems during the course of the work, and this has triggered new research efforts. In some cases these problems have been pure obstacles, and as soon as they have been solved we have returned to the original track. In other cases, the problems we have encountered have turned out to be of interest by themselves, and the results have been published on its own merits. The idea to combine a microlens array with a microfluidic system, which was a result from the collaboration between the Ilmenau and Göteborg groups is an example of this cause of events.

In other cases, some of the work from the proposal have not been conducted. Two examples of this was our intention to produce a switchable microlens arrays. This idea was published by another group before we had time to conduct the research. Further, we have not produce phase modulators based on the geometrical phase, as originally stated in the proposal. Again, our alternative work described above was more timely and exciting.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

The work within the SPANAS CRP has been extremely useful and triggered a lot of activities that exceeds the SPANAS activity both with respect of financial support and time frames. For example, the RNL and Göteborg groups were invited to participate in a STREP (ATOM-3D), in which also the two NOMSAN group were involved. Further, the RNL and Göteborg groups are now members of a newly launched COST activities. In this context one should also mention that the joint activities within the four participating groups has triggered many interesting collaborative efforts that will continue for many years. More specifically the four groups report the following:

Göteborg:The activities in the field of optical manipulation has expanded rapidly during the time of the SPANAS project. The support from SONS was the first major external funding to this activity, and has been acting as a seeding for additional support. Now, the group has obtained several grants both from national and international agencies. Further, the group has emerged as a key player when the Faculty of Sciences at Göteborg University started a program to increase interdisciplinary research.

RNL: The Eurocores funding has convinced the Danish national research councils to support the development of our biophotonics workstation activities in a very focussed way. In addition the PI, Jesper Glückstad, has been invited to join the management committees of two out of four EU COST networks currently being launched.

Durham: The SPANAS work has enabled a whole new research avenue at Durham. We are in the process of continuing this funding through grant applications. Furthermore, in the UK research studentships are awarded on the basis of grants and we therefore have been allocated 2 research studentships because of the SONS funding. One of these students is half way through his studies and the other will start in Oct 2008 to continue this work. Finally, the work on high speed image processing has produced much interest in the micromanipulation community and we are in the process of setting up a spin-out company from the University to commercialise this work. We already have 1 order for a product and 2 more being negotiated.

Ilmenau: There are two new research projects which were started according to the work of the CRP. Financial support is provided by the " German Federal Ministry of Education and Research" (BMBF project "Innosens") and the "Thuringian Ministry of Education and the Arts" (TKM, project "mikrooptische Pinzette"). Both projects are related to optical manipulation in micro fluidic systems. Further international EU funded RP are in preparation.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

We foresee a great potential in the research area where optical techniques are developed for research within the lifesciences. The major problem is that it generally is a very long way from an original idea within optics research to an experiment where a newly developed technique is used in a real biological experiment, and finally published in a high impact biological journal. Research in this field always faces the risk to fall between chairs, where support is neither given from the physics side or the biology side. We here see a great opportunity for ESF to act as an agency to support research that links two research fields which traditionally is seen as been very far apart. It is then very important to give support on a long time scale in order to give time both for development of new techniques, and then apply them on real biological systems. It is only after a successful demonstration by a leading biologist that a new experimental technique will be accepted and spread within the life science community.

On the optics side, one of the major challenges of optical tweezing systems is related to the handling of the complex optical systems. One straight forward result of our research activities demonstrates the possibility to significantly improve this situation by integration of optical functionality into microfluidic channel systems. The potential of resulting micro-opto-fluidic systems will be a very significant area of research in the field. This is related to the complex

topic of the fabrication of integrated optical microsystems incorporating complex hybrid functionality. Recent trends in ultra high precision mechanical microfabrication will have a strong impact in this field.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

On the whole the programme has been excellent. A major advantage has been that the structure of Eurocores has given us a large amount of flexibility to pursue new areas as the research has developed. This has meant that, on the whole, the work we have done has ended up being even more exciting than in the original proposal.
Being members of a CRP in the EUROCORES Programme have triggered fast and informal collaboration as well as exchange of different technologies between the individual IP members. During the project duration of about 3-4 years with various meetings and exchange student exchange between the partners a stimulating interdisciplinary collaboration resulted. It is expected that the good scientific contacts and collaboration will be sustained beyond the end of the CRP.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The only drawback with the EUROCORES program is, as we have mentioned before, the fact that the groups in different countries were all funded differently. In particular, this was a major problem since the different levels of funding were not based on scientific grounds, but merely caused by different policies at the national agencies.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

M. Amberg, A. Oeder, S. Sinzinger, P.J.W. Hands, and G. D. Love: “Tuneable Planar Integrated Optical Systems” Optics Express, accepted (2007).

M. Amberg, A. Oeder, P.J.W. Hands, G. Love, S. Sinzinger, ”Tuneable planar integrated optical systems“, OSA Annual Meeting, 8/10/6 – 12/10/6, Rochester, NY. (Poster Presentaion)

M. Amberg, H. Baitinger, A. Oeder, S. Sinzinger, J. Enger, E. Errikson, M. Errikson, and D. Hanstrop: “Integrated Micro Optics for Multiple Trapping in Micro Fluidic Channels” Optics Letters, in preparation (2007).

M. Amberg, E. Eriksson, J. Enger, M. Goksör, D. Hanstrop, S. Sinzinger „Integrierte Mikrooptik für mikrofluidische Systeme“ Annual Meeting of the GermanOptical Society, Weinheim, 06/06/06-10/06/06. (Talk)

S. Sinzinger, M- Amberg, H. Baitinger, E. Eriksson, J. Enger, D. Hanstorp “Integrated Micro-Optics for Microfluidic Systems”, EOS Annual Meeting, Paris, 16/10-19/10/2006. (Poster Presentation)

Sinzinger, S.; Jahns, J.; Glückstad, J.; Daria, V., Planar microoptical system for correlation and security applications. In: Optical imaging sensors and systems for homeland security applications. (**Book chapter**). Javidi, B. (ed Springer, Berlin, Advanced Sciences and Technologies for Security Applications, 2, p. 339-366 (2006)

Daria, V.R.; Rodrigo, P.J.; Sinzinger, S.; Glückstad, J., Phase-only optical decryption in a planar-integrated micro-optics system, (**Cover page paper**) Opt. Engineering 43, 2223-2227 (2004).

Perch-Nielsen, I.; Eriksson, E.; Goksör, M.; Enger, J.; Rodrigo, P.J.; Hanstor D.; Glückstad, J., Sorting particles in a microfluidic system using SLMreconfigurable intensity patterns. In: Imaging, manipulation, and analysis of biomolecules, cells, and tissues 4. Photonics West 2006: Biomedical Optics 2006, San Jose, CA (US), 21-26 Jan 2006. (International Society for Optical Engineering, Bellingham, 2006) SPIE Proceedings Series, 6088, 60881H (7

Glückstad, J.; Daria, V.R.; Rodrigo, P.J.; Sinzinger, S., Micro-optics for phas only cryptography. SPIE Int. Tech. Group Newslett. on Opt. Inf. Systems. 16 no.1, 9-10 (2005).

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

Durham:

S.A. Tatarkova, D.R. Burnham, A.K.Kirby, G.D. Love, & E.M. Terentjev. "Colloidal Interactions and Transport in Nematic Liquid Crystals." *Phys. Rev. Lett.* **98**, 157801 (2007)

Jonathan Leach, Stephen Keen and Miles J. Padgett, Christopher Saunter and Gordon D. Love. "Direct measurement of the skew angle of the Poynting vector in a helically phased beam." *Optics Express*, **14**(25):11919-11924 (2006)

Philip J.W. Hands, Svetlana A. Tatarkova, Andrew K. Kirby, Gordon D. Love. "Modal liquid crystal devices in optical tweezing: 3D control and oscillating potential wells." *Opt. Express* **14**, 4525-4537 (2006)

S A Tatarkova, D R Burnham, A K Kirby, G D Love. "Anomalous Particle Transport in Nematic Liquid Crystals" Proceedings of Photon06 (IOP), (2006).

Philip J. W. Hands, Svetlana A. Tatarkova, Andrew K. Kirby, Gordon D. Love. "Optical tweezing beam control using liquid crystal adaptive optical elements." *Proc. SPIE* **6326,** 719-726 (2006)

M. Amberg, A. Oeder, P.J.W. Hands, G. Love and S. Sinzinger "Tuneable planar integrated optical systems." Proceedings of the Annual Meeting of the OSA (2006)

Ilmenau:

M. Amberg, and S. Sinzinger: "Design Considerations for efficient planar-optical systems," Opt. Comm. 267, page 74-78 (2006).

S. Sinzinger, M. Amberg, "Planar Optics for the integration of microsystems with optical and fluidic functionality, 3. Workshop "Microtechnology for Chemistry and Biology Laboratories", Ilmenau, 21/02/06-23/2/2006. (invited talk)

M. Amberg, E. Eriksson, J. Enger, M. Goksör, D. Hanstrop, S. Sinzinger „Effiziente Koppelmechanismen für planar integrierte freiraum optische System" Annual Meeting of the GermanOptical Society, Weinheim, 06/06/06-10/06/06. (Poster presentation)

S. Sinzinger, M. Amberg, M. Hoffmann, B. Mitschunas, S. Stoebenau, M. Teschke, „Holographic lithography for the fabrication of complex diffractive elements", ICO Topical Meeting on Optoinformatics/Information Optics 2006, St. Petersburg, Rußland, 4/09/06-7/06/06. (Talk)

S. Sinzinger, M. Amberg, H. Baitinger, „Integrierte Mikrooptik für mikrofluidische Systeme",
13. Heiligenstädter Kolloquium, "Technische Systeme für Biotechnologie und Umwelt", 25/9/06-27/09/06. (Talk)

S. Sinzinger, M. Amberg, A. Oeder, D. Hein, C. Kremin, M. Hoffmann, J. Metze, A. Grodrian, „Integrated Micro-opto-fluidic Systems for Analytics and Manipulation in Cell Cultures", Latsis workshop, Lausanne, 25/06/07-27/06/07 (Talk)

S. Sinzinger, M. Amberg, A. Oeder, D. Hein, „Integrated Micro-opto-fluidic Systems for Optical Manipulation of Cell Cultures", OSA Annual Meeting, Frontiers in Optics, San Jose, CA. USA, 16.9.-20.9.2007.

RNL:
Journal papers:

Dam, J.S.; Rodrigo, P.J.; Perch-Nielsen, I.; Glückstad, J., Opt. Express (200 in press.

Alonzo, C.A.; Rodrigo, P.J.; Glückstad, J., Photon-efficient grey-level image projection by the generalized phase contrast method. New J. Phys. (2007) **9** 132 (15 pages)

Dam, J.S.; Rodrigo, P.J.; Perch-Nielsen, I.; Alonzo, C.A.; Glückstad, J., Computerized ''drag-and-drop'' alignment of GPC-based optical micromanipulation system. Opt. Express (2007) **15** , 1923-1931

Glückstad, J.; Rodrigo, P.J.; Perch-Nielsen, I., Optical 3D manipulation and observation in real-time (**Invited paper**). J. Robotics Mechatronics (2006) (no.6) , 692-697

Rodrigo, P.J.; Perch-Nielsen, I.; Alonzo, C.A.; Glückstad, J., GPC-based opti micromanipulation in 3D real-time using a single spatial light modulator. Opt. Express (2006) **14** , 13107-13112

Perch-Nielsen, I.; Rodrigo, P.J.; Alonzo, C.A.; Glückstad, J., Autonomous an 3D real-time multi-beam manipulation in a microfluidic environment. Opt. Express (2006) **14** , 12199-12205

Rodrigo, P.J.; Perch-Nielsen, I.; Glückstad, J., Three-dimensional forces in GPC-based counterpropagating-beam traps. Opt. Express 14, 5812-5822 (2006).

Rodrigo, P.J.; Perch-Nielsen, I.; Glückstad, J., High-speed phase modulation using the RPC method with a digital micromirror-array device. Opt. Express 5588-5593 (2006).

Glückstad, J.; Rodrigo, P.J.; Perch-Nielsen, I., Drag-and-drop system manipulates microparticles in 3D. SPIE Newsroom - Biomedical Optics and Medical Imaging, vp. (2006).

Sinzinger, S.; Jahns, J.; Glückstad, J.; Daria, V., Planar microoptical system for correlation and security applications. In: Optical imaging sensors and systems for homeland security applications. (**Book chapter**). Javidi, B. (ed Springer, Berlin, Advanced Sciences and Technologies for Security Applications, 2, p. 339-366 (2006)

Glückstad, J.; Perch-Nielsen, I.; Rodrigo, P.J., Micro-biologic applications of real-time interactive 3D optical manipulation. (**Selected paper**). Opt. Photonics News 16, 18 (2005)

Rodrigo, P.J.; Gammelgaard, L.; Bøggild, P.; Perch-Nielsen, I.; Glückstad, J. Actuation of microfabricated tools using multiple GPC-based counterpropagating-beam traps. Opt. Express 13, 6899-6904 (2005).

Perch-Nielsen, I.; Rodrigo, P.J.; Glückstad, J., Real-time interactive 3D manipulation of particles viewed in two orthogonal observation planes. (**Cov page paper**). Opt. Express 13, 2852-2857 (2005).

Arneborg, N.; Siegumfeldt, H.; Andersen, G.H.; Nissen, P.; Daria, V.R.; Rodrigo, P.J.; Glückstad, J., Interactive optical trapping shows that confinement is a determinant of growth in a mixed yeast culture. FEMS Microbiol Lett. 245 **,** 155-159 (2005).

Alonzo, C.A.; Rodrigo, P.J.; Glückstad, J., Helico-conical optical beams: a product of helical and conical phase fronts. (**Cover page paper**) Opt. Express 13, 1749-1760 (2005).

Rodrigo, P.J.; Daria, V.R.; Glückstad, J., Dynamically reconfigurable optical lattices. Opt. Express 13, 1384-1394 (2005).

Glückstad, J.; Daria, V.R.; Rodrigo, P.J.; Sinzinger, S., Micro-optics for phas only cryptography. SPIE Int. Tech. Group Newslett. on Opt. Inf. Systems. 16 no.1, 9-10 (2005).

Rodrigo, P.J.; Daria, V.R.; Glückstad, J., Four-dimensional optical manipulat of colloidal particles. Appl. Phys. Lett. 86, 074103.1-074103.3 (2005).
Rodrigo, P.J.; Daria, V. R., Glückstad, J., Optical manipulation of high- and low-index particles and living cells. (**Selected paper**). Optics & Photonics News 15, 20 (2004).

Glückstad, J., The Generalised Phase Contrast method. (Risø National Laboratory, Roskilde) 322 p. (DSc. thesis) (2004).

Rodrigo, P. J.; Daria, V. R.; and Glückstad, J., Real-time three-dimensional optical micro-manipulation of multiple particles and living cells, Opt. Letters 29, 2270-2272 (2004).

Glückstad, J.; Daria, V.R.; Rodrigo, P.J.; Decrypting binary phase patterns b amplitude. Opt. Engineering 43, 2250-2258 (2004)

Daria, V.R.; Rodrigo, P.J.; Sinzinger, S.; Glückstad, J., Phase-only optical decryption in a planar-integrated micro-optics system, (**Cover page paper**) Opt. Engineering 43, 2223-2227 (2004).
Rodrigo, P.J. , Daria, V.R., J. Glückstad, Real-time interactive optical micromanipulation of a mixture of high-and low-index particles, (**Cover pag paper**). Opt. Express 12, 1417-1425 (2004).

Daria, V.R.; Rodrigo, P.J.; Glückstad, J., Dynamic formation of optically trapped microstructure arrays for biosensor applications. Biosensors and Bioelectronics (Special issue on Micro and Nano Bioengineering) 19, 11, 143 1444 (2004).

Daria, V.R.; Rodrigo, P.J.; Glückstad, J., Programmable complex field coupli to high-order guided modes of micro-structured fibres. Opt. Comm. 232, 22 237 (2004).

Glückstad, J., Sorting particles with light. (**Invited paper**). Nature Materials 9-10 (2004).

Daria, V.R.; Rodrigo, P.J.; Glückstad, J., Dynamic array of dark optical traps Appl. Physics Letters 84, 323-325 (2004).

Conference papers:

Glückstad, J.; Rodrigo, P.J.; Perch-Nielsen, I.; Alonzo, C., Track and trap in (**Invited Paper**). In: Proceedings. Optical pattern recognition 18, Orlando, (US), 9-10 Apr 2007. Casasent, D.P.; Chao, T.-H. (eds.), (International Society for Optical Engineering, Bellingham, 2007) (SPIE Proceedings Serie 6574) 657403 (9 pages).

Alonzo, C.; Rodrigo, P.J.; Perch-Nielsen, I.; Glückstad, J., Three-dimensiona intensity distribution of helico-conical optical beams. In: Complex light and optical forces. Photonics West 2007: Biomedical Optics (BiOS), San Jose, CA (US), 20-25 Jan 2007. Andrews, D.L.; Galvez, E.J.; Nienhuis, G. (eds.), (International Society for Optical Engineering, Bellingham, 2007) (SPIE Proceedings Series, 6483) 64830O (9 pages)

Rodrigo, P.J.; Perch-Nielsen, I.; Alonzo, C.; Glückstad, J., Single-SLM 3D interactive micromanipulation based on the generalized phase contrast (GP approach. In: Imaging, manipulation, and analysis of biomolecules, cells, a tissues V. Photonics West 2007: Biomedical Optics (BiOS), San Jose, CA (U 20-25 Jan 2007. Farkas, D.L.; Leif, R.C.; Nicolau, D.V. (eds.), (Internationa Society for Optical Engineering, Bellingham, 2007) (SPIE Proceedings Serie 6441) 644110 (7 pages)

Rodrigo, P.J.; Perch-Nielsen, I.; Glückstad, J., GPC-based counterpropagatin beam traps with unequally sized intensity profiles. In: Optical trapping and optical micromanipulation 3. SPIE annual meeting: Optics and Photonics 200 San Diego (US), 21 Aug. 2006. (International Society for Optical Engineerin Bellingham, 2006) SPIE Proceedings Series 6326, 632612Z (5 p.)

Perch-Nielsen, I.; Rodrigo, P.J.; Glückstad, J., Manipulation of yeast cells in a microfluidic channel using the GPC-based optical trapping system. In: Optical trapping and optical micromanipulation 3. SPIE annual meeting: Optics and Photonics 2006, San Diego (US), 21 Aug. 2006. (International Society for Optical Engineering, Bellingham, 2006) SPIE Proceedings Series 6326, 63261X (6 p.)

Glückstad, J., Optical manipulation within the SPANAS-project (**Invited talk** Book of abstracts. SONS conference 2006, San Giuliano Terme (IT), 28 Jun Jul 2006. (European Science Foundation Collaborative Research, 2006, p. 9.
Perch-Nielsen, I.; Eriksson, E.; Goksör, M.; Enger, J.; Rodrigo, P.J.; Hanstor D.; Glückstad, J., Sorting particles in a microfluidic system using SLMreconfigurable intensity patterns. In: Imaging, manipulation, and analysis of biomolecules, cells, and tissues 4. Photonics West 2006: Biomedical Optics
2006, San Jose, CA (US), 21-26 Jan 2006. (International Society for Optical Engineering, Bellingham, 2006) SPIE Proceedings Series, 6088, 60881H (7

Rodrigo, P.J.; Gammelgaard, L.; Bøggild, P.; Perch-Nielsen, I.; Glückstad, J Optically driven microtools fabricated by UV lithography and RIE. In: Nanomanipulation with light 2. Photonics West 2006: Optoelectronics 2006, San Jose, CA (US), 21-26 Jan 2006. (International Society for Optical Engineering, Bellingham, 2006) SPIE Proceedings Series, 6131, 61310B (5 p

Glückstad, J.; Rodrigo, P.J.; Perch-Nielsen, I., A 3D interactive optical manipulation platform. (**SPIE Best Paper Award**) In: Optomechatronic actuators and manipulation. Optomechatronic technologies 2005, Sapporo (JP), 4-7 Dec 2005. (International Society for Optical Engineering, Bellingha 2005) SPIE Proceedings Series 6048, p. 75-84

Glückstad, J.; Rodrigo, P.J.; Nielsen I, GPC-driven optical micro-manipulatio (**Invited paper**). In: Optical Trapping and Optical Micromanipulation II, Sa Diego, CA (US), International Society for Optical Engineering, Bellingham, 2005, SPIE Proceedings Series 5930, p. 248-255.

Rodrigo, P.J.; Alonzo, C.; Glückstad, J.; Generation of spiral optical beams b spatial light modulator. In: Optical Trapping and Optical Micromanipulation I San Diego, CA (US), International Society for Optical Engineering, Bellingha 2005, SPIE Proceedings Series 5930, p. 486-491

Glückstad, J., GPC-based optical manipulation (**Invited paper**). In: Adaptiv optics: Analysis and methods; Computational optical sensing and imaging; Information photonics; Signal recovery and synthesis topical meetings on C ROM. Conference, Charlotte, NC (US), 6-9 Jun 2005. (Optical Society of Americal, Washington, DC (US), 2005) 3 p.

Glückstad, J., 4D optical multi-beam manipulation (**Invited paper**). In: Optical pattern recognition 16. Conference, Orlando, FL (US), International Society for Optical Engineering, Bellingham, 2005, SPIE Proceedings Series 5816, p. 32-38.

Glückstad, J.; Rodrigo, P.J.; Daria, V.R., H. Siegumfeldt, P. Nissen and N. Arnfeldt, Optical micro-manipulation of mixed yeast cell populations for analyzing growth behaviour In: Manipulation and Analysis of Biomolecules, Cells and Tissues, San Jose, CA (US), International Society for Optical Engineering, Bellingham, 2005, SPIE Proceedings Series, 5699.

Glückstad, J.; Rodrigo, P.J.; Daria, V.R., 4D multi-beam optical manipulation based on the Generalised Phase Contrast method. In: Nanomanipulation wit light. Conference, San Jose, CA (US), International Society for Optical Engineering, Bellingham, 2005, SPIE Proceedings Series, 5736, p. 30-36

Rodrigo, P.J., Daria, V.R.; Glückstad, J., Multiple dual-beam traps for threedimensional position control of particles (**Invited paper**). In: Optical Trapp and Optical Micromanipulation, Denver, CO (US), International Society forOptical Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 5514 336-330.

Glückstad, J.; Daria V.R., Rodrigo, P.J., State-of-the-art in Generalized Phas Contrast driven optical micromanipulation. In: Optical trapping and Optical Micromanipulation, Denver, CO (US), International Society for Optical Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 5514 p. 117-125.

Daria, V.R.; Rodrigo, P.J., Glückstad, J., Integrated miniaturized laboratorie using dynamic multiple-beam optical manipulators. In: Optical Trapping and Optical micromanipulation, Denver, CO (US), International Society for Optic Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 5514 p. 48-54

Glückstad, J.; Rodrigo, P.J., Daria, V.R., Dynamic 3D particle position contro Generalized Phase Contrast based optical trap arrays. In: Biophotonics Micro and Nano-imaging, Photonics Europe, Strassbourg (FR), International Societ for Optical Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 54 p. 21-26.

Rodrigo, P.J., Daria, V.R.; Glückstad, J.; Interactive optical micromanipulatio

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Glückstad, J.; Daria, Rodrigo, P.J., An interactive microscope for microfluidic research. In: Optics in computing 2004. EOS topical meeting, Engelberg (CH 21-23 Apr 2004. (European Optical Society, Hannover, 2004) p. 153-154.

Rodrigo, P.J., Daria, V.R.; Glückstad, J.; Array of optical tweezers with individual beam-steering and polarization control. In: Manipulation and Analysis of Biomolecules, Cells and Tissues, San Jose, CA (US), Internationa Society for Optical Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 5322.

Daria, V.R.; Rodrigo, P.J., Glückstad, J.; Multiple doughnut beams for trappi and dynamic manipulation of low-index microstructures. In: Manipulation an Analysis of Biomolecules, Cells and Tissues, San Jose, CA (US), Internationa Society for Optical Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 5322.

Daria, V.R.; Rodrigo, P.J., Glückstad, J.; Far-field technique for tunable coupling to high-order guided modes of photonic crystal fibers. In: Photonic crystal materials and devices II, San Jose, CA (US), International Society fo Optical Engineering, Bellingham, WA, 2004, SPIE Proceedings Series, 5360.

Daria, V.R.; Rodrigo, P.J., Glückstad, J., Active microscopy via dynamic photonic manipulation of colloidal structures (**Invited presentation**). In: International Conference on Nanophotonics (ICONA 2004), Kanagawa (JP), 12 Jan 2004. (Osaka University, Osaka, 2004) p. 5-6.

Göteborg:
A microfluidic system enabling Raman measurements of the oxygenation cycle in single optically trapped red blood cells, K. Ramser, J. Enger, M. Goksör, D. Hanstorp D, K. Logg and M. Käll, Lab on a Chip **5** (2005) 431.

Ex-situ imaging of permanent 3D structures created using holographic optical tweezers, P. Jordan, J. Cooper, M. Goksör, D. Hanstorp, A. Wright, J. Girkin, P. Blackburn, N. Issacs and M. Padgett, Accepted by Lab-on-A-Chip 5 (2005) 1224.

A microfluidic system for analyzing rapid and reversible cytological alterations in single cells upon environmental changes, Emma Eriksson, Jonas Enger, Bodil Nordlander, Nika Erjavec, Kerstin Ramser, Mattias Goksör, Stefan Hohmann, Thomas Nyström and Dag Hanstorp,. Lab-on-a-Chip. **7**, (2007) 71 – 76.

Optical manipulation and microfluidics for studies of single cell dynamics E Eriksson, J Scrimgeour, AGranéli, K. Ramser, R. Wellander, J Enger, D. Hanstorp and M Goksör, J. Opt. A In press

A combined micro-resonance Raman and absorption set-up enabling *in vivo* studies under varying physiological conditions: The nerve globin in the nerve cord of *Aphrodite aculeate,* K. Ramser, W. Wenseleers, S. Dewilde, S. Van Doorslaer, L. Moens and D. Hanstorp, Journal of Biochemical and Biomedical Methods, In press

Micro Resonance Raman study of optically trapped Escherichia coli cells overexpressing human Neuroglobin, K. Ramser, W. Wenseleers, S. Dewilde, S. Van Doorslaer, L. Moens and D. Hanstorp, Journal of Biomedical Optics Accepted,

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Ilmenau:

Newspaper: Freies Wort (14/04/07); Article about optical trapping at the IPs institute in Ilmenau

Newspaper: Thüringer Allgemeine (14/04/07); Article about optical trapping at the IPs institute in Ilmenau

RNL:
March 2007: Feature article in New Scientist, 7 March 2007.
March 2007: Paper on computerized "drag-and-drop" alignment of counterpropagating beams is Reprinted in Virtual Journal for Biomedical Optics.
Jan 2007: Feature article on the cover of the Danish Science Ministry website.
Jan 2007: Paper on GPC-based 3D real-time optical trapping system using a single SLM is Reprinted in Virtual Journal for Biomedical Optics.
Jan 2007: Paper on GPC-based real-time, autonomous optical trapping in a microfluidic system is Reprinted in Virtual Journal for Biomedical Optics.
Jan 2007: Radio Program on DR P1 Videnskabens Verden, 20 January 2007.
Nov 2006: Feature article in "Illustreret Videnskab", 9 November 2006.
Aug 2006: Two feature articles in "Ingeniøren", 4 August 2006.
Aug 2006: Feature article in "Politiken", 2 August 2006.
July 2006: Paper on 3D forces in GPC-based CP-beam traps is Reprinted in Virtual Journal for Biomedical Optics.
June 2006: Paper on 3D forces in GPC-based CP-beam traps is Reprinted in Virtual Journal of Biological Physics Research.
May 2006: Our research work is featured on Denmark's official website.
May 2006: Brief coverage in the DTU magazine Dynamo.
April 2006: "Drag-and-drop system manipulates microparticles in 3D," SPIE Newsroom.
March 2006: French Embassy news about our work http://www.bulletinselectroniques.

com/actualites/32450.htm.
Feb 2006: Feature article by The Danish Research Councils, 3 February 2006.
Jan 2006: J. Glückstad became Research Professor at Risø and Guest Professor at Lund Institute of Technology, Sweden.
Jan 2006: Feature article in "Politiken", 7 January 2006.
Dec 2005: Best Paper Award at ISOT 2005: SPIE International Symposium on Optomechatronic Technologies, Dec. 2005, Sapporo Convention Center, Japan.
Dec 2005: Coverage in the European Optical Society newsletter.
7 Nov 2005: Jesper Glückstad was awarded the Danish "Scientist of the Year, 2005" award from dir. Ib Henriksens Foundation at a ceremony held at the Hotel D'Angleterre in Copenhagen.
The Danish Research Councils: one of eight feature stories.
Aug 2005: This month's issue of The Scientist magazine features our work.
July 2005: This month's issue of Optics & Photonics News magazine features our work.
June 2005: Paper on Real-time interactive 3D manipulation of particles observed in two orthogonal observation planes is Reprinted in Virtual Journal of Biological Physics Research.
May 2005: Paper on Dynamically reconfigurable optical lattices is Reprinted in Virtual Journal of Biological Physics Research.
May 2005: Opto & Laser Europe, "Optical manipulation plays tricks with particles."
May 2005: Laser Focus World writes a news article featuring our Helico-Conical Optical Beams.
April 2005: Danish National Television, DR2 program: "Einstein's century" broadcasted 19 April.
April 2005: Technology Research News, "Spiral laser beam demoed."
Optics.org writes a feature article on our 4D optical micromanipulation system.
March 2005: Feature article in "Politiken", 13 March 2005.
February 2005: Paper on Real-time three-dimensional optical micromanipulation of multiple particles and living cells is Reprinted in Virtual Journal of Biological Physics Research.
GPC-based multi-beam optical manipulation is among the top 5 technical innovations in Denmark for 2004.
Doctor of Science Thesis (Dr. Technices; Habilitation): Jesper Glückstad successfully defended his dissertation at the Technical University of Denmark; 13 December 2004.
Royal state-visit to Japan: Jesper Glückstad was invited to give a speech as part of the Danish research and business delegation attending the affair; 15-19 November 2004.
Swedish Engineering news, "NyTeknik" - 7 Sept 2004"
Danish Ministry of Foreign Affairs IT News - 23 August 2004
Feature article in "Politiken- 14 Aug 2004"
Risø News - 9 Aug 2004

Feature article in "The Copenhagen Post - 6 Aug 2004"
Feature article in "Ingenioren - 6 Aug 2004"
June 2004: TRNMAG.COM The Latest Technology Research News, "Laser tweezer grabs varied specks"
May 2004: MICRO/NANO, "Dark optical traps offer advantages"
May 2004: Paper on Real-time interactive optical micromanipulation of a mixture of high-and low-index particles is Reprinted in Virtual Journal of Biological Physics Research. (Link)
April 2004: Risø-Nyt no.1 2004
March 2004: Japanese OE Magazine

1 D. Patents and industry collaborations

Durham

A spin-out company to be formed – see section 5 above.

RNL:
Glückstad, J. US 60/521,318.
Glückstad, J. WO2004113993
Glückstad, J. WO2005096115
Glückstad, J. US provisional 2005
Glückstad, J. US provisional 2006

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

SPANAS Kick-Off Meeting. Göteborg, Sweden. March 2004.

Eurocores workshop, “Applications of Optical Tweezers.” Greenock, U.K. Sept. 2004.

Meeting at the SPIE Meeting on Optical Tweezing and Micromanipulation (SPIE Annual Meeting, July 2005): attended by the Durham and Risø group SPANAS Partners Annual Meeting. Durham, UK. Apr. 2006

Collaborative visit of Andreas Oeder (Ilmenau) to Durham for 4 weeks. July – Aug 2006.

Collaborative visit of Gordon Love (Durham) to Riso for 1 week. Aug. 2006.

Student Exchange Gothenburg-Ilmenau: Lab work of a student in the Gothenburg’s lab (5 weeks stay)

Cooperated Experiments at the Gothenburg’s lab of Martin Amberg (1 week stay)

Mutual visits between Göteborg and Risö

1 F. Participation in other conferences

Please list only the most relevant

SPIE Annual Meeting. . “Optical tweezing and micromanipulation.” San Diego, USA. July 2006

Summer school “Imaging, Communication, and Disorder” Institut d'Etudes Scientifiques de Cargèse, France, June 2006

Photon06: The Institute of Physics Conference on Optics and Photonics. Manchester, Sept. 2006.

Annual Meeting: Deutsche Gesellschaft für angewandte Optik (Weinheim, 06/06/06-10/06/06 and Heringsdorf 29/05/07-02/06/07) => talk

SONS Meeting in PISA (Italy) (29/06/06-01/07/06) => talk

EOS annual meeting Paris (France)(16/1006-19/10/06) => poster presentation

SONS Meeting in Straßburg => poster presentation

Workshop “Mikrotechnology for Chemistry and Biology Laboratories” Ilmenau (Germany) (21/02-23/022006) => invited talk

Eurocores workshop, “Applications of Optical Tweezers.” Greenock, UK. Sept. 2004.

ESF co-sponsored summerschool and workshop: “Physics in Life” coorganised by Jesper Glückstad and held during one week in Aug. 2005 at Humlebaek, Denmark.

Meeting at the SPIE Meeting on Optical Tweezing and Micromanipulation (SPIE Annual Meeting, July 2005): attended by the Durham and Risø group SPANAS Partners Annual Meeting. Durham, UK. Apr. 2006

Optical manipulation within the SPANAS-project (invited presentation). In: Book of abstracts. SONS conference 2006, San Giuliano Terme (IT), 28 Jun - 1 Jul 2006. European Science Foundation Collaborative Research. Collaborative visit of Gordon Love (Durham) to RNL for 1 week. Aug. 2006.

3D drag-and-drop biophotonics workstation (Invited Presentation). In: Book of abstracts. ESF-FWF conference: Trends in optical

micromanipulation, Ötz Valley (AT), 4-9 Feb 2007. European Science Foundation, 2007

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

Durham:
Dr. Svetlana Tatarkova, Senior Research Associate. 1/4/4 to 31/3/8

Ilmenau:
100% Martin Amberg, Ph.D. student, 05/01/04-04/01/08 funded by different project in period 01/06/06-31/05/07

RNL:
Postdoc: Ivan R. Perch-Nielsen

Göteborg:

Ph. D. Jonas Enger

EUROPEAN SCIENCE FOUNDATION

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (to be completed with information form the ESF database)	
1. General information	
Project Reference Number:	02-PE-SONS-045
Acronym / Short Title:	SSA-TMN
Full Title:	(Supra-)Self-Assemblies of Transition Metal Nanoclusters
Project Leader name:	Alessandro Fortunelli
Project Leader affiliation:	IPCF-CNR, Pisa, Italy
Institutional home page (URL):	www.ipcf.cnr.it
Project-related home page (URL):	h2.ipcf.cnr.it/alex/ssatmn.html
Reporting period:	from 01/01/2006 to 30/04/2007
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)	
IP 1	
Principal Investigator: Alessandro Fortunelli, IPCF-CNR, Pisa, Italy	
Total funding amount of the IP: 159600,00 Euros	
IP 2	
Principal Investigator: Riccardo Ferrando, INFM, Genova, Italy	
Total funding amount of the IP: 142800,00 Euros	
IP 3	
Principal Investigator: Gilles Renaud, DRFMC-CEA, Grenoble, France	
Total funding amount of the IP: 122400,00 Euros	
AP 1	
Principal Investigator: Claude Henry, CRMCN-CNRS, Marseille, France	

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The structure of metal nanoclusters is a subject of active research. The aim is to understand the cross-over among structural motifs due to thermodynamic or kinetic effects, and to fully understand the underlying physics in order to make accurate theoretical predictions. In this context, magic clusters have potential advantages in many applications because they are more stable than other clusters, so that they represent basins of attraction in the growth process, and can thus be easily produced and used for their peculiar properties or as building blocks of more complex materials.

(1) Two novel theoretical protocols for the prediction of the structure of metal clusters (in general, nanosystems presenting structural phase transitions) have been developed: (a) a density-functional basin-hopping (DF-BH) algorithm [23], one of the first examples in the literature in which global optimization techniques are coupled with accurate first-principles approaches; (2) a hybrid empirical potential/density-functional algorithm [24,25] combined for the first time in the literature with structure recognition algorithms [37]. These two approaches are complementary, and provide a general methodological framework in which to pursue the search for magic structures. They have allowed us to: (a) predict the first oxide surface magic clusters [33,55], i.e., the first examples of magic metal clusters adsorbed on a (defected) oxide surface; (b) predict a new family of bimetallic magic cluster structures [4], i.e., core-shell silver-nickel and silver-copper structures which have a polyicosahedral character, special stability, high melting temperatures, and large HOMO-LUMO gaps (the Ag-Ni alloys are also magnetic in their ground state); (c) accurately predict epitaxy and defect formation of deposited metal clusters for the first time of reasonable sizes [29].

(2) A set of computer programs has been developed for the study of the growth process of metal clusters deposited on a support (such as the surface of an oxide). To our knowledge, this represents the first software in which the growth process can be studied in a thorough way, linking first-principles calculations based on sophisticated quantum mechanical algorithms to simplified descriptions based on computationally inexpensive, yet accurate atom-atom potentials, and cross-fertilizing the investigation of static structures (in which the search for the global minima, i.e. the most favorable structure from the energetic point of view, is performed via global-optimization algorithms) with the study of dynamic processes, obtained in the simplest cases via classical Molecular Dynamics, and rescaling the time scale in more complex instances via Accelerated MD and kinetic Monte-Carlo approaches. Melting phenomena [13] are also within the reach of the software. This software also has features of general validity, and can be applied to growth phenomena in other fields. This has has allowed us to obtain a fair agreement between theoretical [12,28] and experimental [5,6,16,43] results on the growth of metal clusters on MgO(100), underlining the important of diffusion process of small metal clusters.

Three nanostructured surfaces have been investigated:

(3) An inhomogenously strained Ag(001) surface arising from an underlying square misfit dislocation network of 10 nm periodicity buried at the interface between a 5nm-thick Ag film and

a MgO(001) substrate, as revealed by *in situ* GISAXS and confirmed by MD simulations [18], on which the self-organized growth of Co nanoparticles was achieved (with the Co clusters growing on top of the dislocation crossing lines). The periodic surface strain field induced by a misfit dislocation network buried as far as 5 nm below an Ag(001) surface allows controlling the growth of Co clusters at room temperature. We believe that this method could be used for many different systems, metal thin films being favoured with respect to semiconductor ones because of the dislocation mobility necessary to reach the equilibrium state, and is extremely promising also for the "reverse" oxide-on-metal systems, as shown by preliminary results on the CoO/Ag(100) [47] and MgO(Mo(100) systems.

(4) Thin films of alumina grown on the $Ni_3Al(111)$ alloy present nanopatterns with 4.1 nm periodicity [49] extending for macroscopic (1 cm^2) distances [54]. Their characteristics as ideal templates for nanostructured growth have been tested and impressively verified [50,53] by studying nucleation and growth of monometallic Au and Pd clusters as well as bimetallic Au-Pd clusters onto them. Pd particles nucleate exclusively on the sites of the 4.1 nm superstructure, forming a highly ordered (supra-organized) and size-selected cluster array. Moreover, by post-depositing Au on the ordered Pd cluster arrays, the Au atoms are captured by the Pd clusters and form bimetallic Au-Pd particles, potentially of great interest in the field of catalysis, as shown by determining the adsorption energy and the diffusion energy of CO on the alumina film. It has thus been shown that size, composition and hence catalytic properties of bimetallic Au-Pd clusters supported on $Al_2O_3/Ni_3Al(111)$ can in principle be controlled independently.

(5) A complete structural characterization of several titanium oxide phases grown on a (111) Pt surface has been achieved through a joint experimental and theoretical effort [34-36]: a *zigzag*-like incommensurate phase, a *kagomé*-like incommensurate phase and a *wagon-wheel*-like commensurate phase. For all these three TiO_x phases, the DF structural models have been validated by comparing simulated and experimental UV and XAS spectra. In the *kagomé*-like and *wagon-wheel*-like TiO_x phases, the "holes" created by Ti vacancies constitute potential trapping and nucleation centers for the growth of adsorbed metal clusters, whereas the regular patterns extend for macroscopic distances and seem to be stable to ambient conditions. These materials are thus extremely promising as naturally nano-patterned templates for the growth of not only metal clusters, but also (bio)organic and inorganic species.

Collaboration among research groups has been substantial, and might have not arisen outside the CRP. Point (1) and (2) have been obtained through a very strict collaboration between IP1 and IP2, with the experimental results of (and many discussions with) IP3 and AP1 as inspiration. Point (3) arose from a collaboration between IP3 and AP1, while point (4) has also benefited from this collaboration. From the point of view of IP1, point (5) was inspired by and chosen as a more approachable system (to be studied preliminarily) than point (4).

The topic of surface nanopatterning and magic clusters as tools for orienting the growth and obtaining narrow size and shape distributions (a novel research topic as long as the participating groups are concerned) has been initiated within SSA-TMN, and has originated the thematic Workshop on Surface Nanopatterning and the Summer School on Metal Clusters and Surfaces, apart from SSA-TMN-follow-up research activities. Many questions have arisen while dealing with this topic, especially as ultra-thin oxide films on metal supports presenting regular arrays of "holes" acting as trapping centres are concerned, such as: the issue of the charge of the metal clusters [48] in connection with the underlying metal support, and the decisive influence of the surface defect on the metal cluster structure. The search of magic clusters adsorbed on oxide defect trapping centres is in itself a new idea.

4. What did you not achieve in the CRP and why? (max 1 p.)
Please use the original proposal as reference and explain any deviations from the work plan

No major deviations have been taken from the original work plan. As originally foreseen, experiments and simulations on the growth and supra-organization of metal clusters on oxide surfaces have been conducted and the experimental and theoretical tools for monitoring and characterizing static and dynamic processes have been developed or refined. The good agreement between theory and experiment represented at the same time a cross-check and a mutual stimulus to both. Rather, a qualification and a shift of emphasis on surface nanopatterning and magic clusters as tools for orienting the growth and obtaining narrow size and shape distributions have emerged. In view of this novel view point the work plan has mostly focused on the structural aspects of SSA-TMN, the investigation of the properties of metal clusters being started but somewhat delayed till fully monodisperse systems could be obtained. Moreover, as surface nanopatterning and magic clusters involve systems much more complex than the model ones originally foreseen and also clarified within the project, their thorough characterisation has started but it has not been yet fully achieved. In perspective, what remains to be done is thus to complete the work conducted within SSA-TMN on nanopatterned surfaces and magic clusters, which will also allow one to gradually shift from basic research to real-world applications.
In detail, three main points deserve further investigation:

(1) A wealth of theoretical and experimental information exists on MgO(100), its surface defects and their influence on the metal cluster growth. Still, details such as the abundance of each type of defects as a function of the surface preparation method and the issue of charging of both the surface and metal clusters grown on it (especially for ultra-thin films) deserves some more research effort as they are important in view of the use of this system in applications.
(2) Many of the most promising nano-structured oxide substrates, a prototypical example being $Al_2O_3/Ni_3Al(111)$, present huge unit cells, and thus great difficulties to accurate theoretical simulations, in addition to the problems connected with their experimental investigation. While research on these substrates and their structural characterisation has already begun and in some cases has already been achieved, it simply represents the starting point of the SSA-TMN protocol, and a need of novel predictive theoretical tools for metal cluster growth on substrates with such large unit cells (and possibly with an underlying metal support) is strongly felt.
(3) Once structural issues are fully clarified, research on structure-property relationships can be investigated in more depth than done until now. Unique opportunities in this respect are provided by the cluster size, shape and supra-organization selection in the field of mechanistic studies of catalytic reactions, gas sensing, optical traps, and others.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

The project PSONOS (Particle Self-Organization on Nanostructured Oxide Surfaces) has been presented within the NMP Priority of FP7, topic "Self-organization and self-assembly". The main idea of this project is based on research activities on nanopatterned oxide surfaces which have been originated within the SSA-TMN project and its SONS networking activities, such as the "Workshop on Surface Nanopatterning" and the "Summer School on Metal Clusters and Surfaces", but expanding the SSA-TMN partnership to a much larger set of research groups.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

In my opinion, the most challenging and promising perspectives in my field of research arise from the interaction of traditional surface science with biological and/or organic expertise (to use a synthetic expression: "biological surface science"). Despite recent developments, these two fields of expertise have not interacted much, whereas from an exchange of knowledge and synthetic and characterization tools many benefits can derive for both. In this context, in particular, it is to be expected that the use of (naturally) nanostructured surfaces will be decisive. Programmes aimed at promoting this interaction would thus be very beneficial.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

The added value to our groups for being part of the SONS Programme was the opportunity of being in contact with other groups working on similar but not entirely overlapping topics, whence the possibility of expanding personal view points into a general context, and stimulating contacts to pursue novel research avenues.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

In our opinion, the main issue of EUROCORES programmes concerns the financial aspects, with the complications associated with the fact that the ESF manages these Programmes, but the funds are distributed by the various several National Funding Agencies, so that any inconsistency within this multi-national set-up translates into funding problems for the research groups.
As for the positive aspects, we really appreciated the reasonable speed and full transparency of the reviewing process, the fact that proposal forms were limited to the essential and not burdened with unnecessary requirements, and that – once the funds were granted – reporting was kept to a minimum still sufficient to monitor the progress of the project. We would definitely recommend to keep these positive aspects in future activities.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

The numbering coincides with that of the full list below.

[3] Aprà E., Baletto F., Ferrando R., Fortunelli A. "Amorphization mechanism of icosahedral metal nanoclusters" Phys. Rev. Lett., 93, 065502 (2004)

[4] Rossi G., Rapallo A., Mottet C., Baletto F., Fortunelli A., Ferrando R. "Magic polyicosahedral core-shell nanoclusters" Phys. Rev. Lett., 93, 105503 (2004)

[6] Renaud G., Henry C. et al., "Quantitative analysis of grazing incidence small-angle x-ray scattering: Pd/MgO(001) growth", Phys. Rev. B 69, 035411 (2004)

[7] Rapallo A., Rossi G., Ferrando R., Fortunelli A., Curley B. C., Lloyd L. D., Tarbuck G. M., Johnston R. L. "Global optimization of bimetallic cluster structures. I. Size-mismatched Ag-Cu, Ag-Ni, and Au-Cu systems" J. Chem. Phys., 122, 194308 (2005)

[8] Rapallo A., Rossi G., Ferrando R., Fortunelli A., Curley B. C., Lloyd L. D., Johnston R. L. "Global optimization of bimetallic cluster structures. II. Size-matched Ag-Pd, Ag-Au, and Pd-Pt systems" J. Chem. Phys., 122, 194309 (2005)

[10] Ferrando R., Fortunelli A., Rossi G. "Quantum effects on the structure of pure and binary metal nanoclusters" Phys. Rev. B, 72, 085449 (2005)

[11] Ferrando R., Fortunelli A., Rossi G. "Quantum effects on the structure of pure and binary metal nanoclusters" Virtual J. Nanosci. Nanotech., 12, Iss. 10 (2005)

[12] Barcaro G., Fortunelli A., Nita F., Ferrando R. "Diffusion of palladium clusters on magnesium oxide" Phys. Rev. Lett., 95, 246103 (2005)

[13] C. Mottet, Rossi G., F. Baletto, Ferrando R., "Single impurity effect on the melting of nanoclusters" Phys. Rev. Lett., 95, 035501 (2005)

[18] Leroy, F., G. Renaud, A. Letoublon, R. Lazzari, C. Mottet and J. Goniakowski. "Self-organized growth of nanoparticles on a surface patterned by a buried dislocation network." Physical Review Letters **95**: 185501. (2005)

[23] E. Aprà, R. Ferrando and A. Fortunelli, "Density-functional global optimization of gold nanoclusters", Phys. Rev. B 73, 205414 (2006)

[24] G. Barcaro, A. Fortunelli, G. Rossi, F. Nita, R. Ferrando, "Electronic and Structural Shell Closure in AgCu and AuCu Nanoclusters", *J. Phys. Chem. B*, 110, 23197 – 23203 (2006)

[29] G. Barcaro, A. Fortunelli, G. Rossi, F. Nita, R. Ferrando, "Epitaxy, Truncations, and Overhangs in Palladium Nanoclusters Adsorbed on MgO(001)", *Phys. Rev. Lett.*, 98, 156101 (2007)

[38] G. Rossi, C. Mottet, F. Nita and R. Ferrando, " Global Optimization Study of Small ($10 < N < 120$) Pd Clusters Supported on MgO(100)", J. Phys. Chem. B 110, 7436 (2006).

[40] G. Rossi, R. Ferrando and C. Mottet "Atomic structure and chemical ordering in PtCo nanoalloys", submitted to Faraday Discussions.

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

[1] Fortunelli A., Velasco A. M. "On the tight-binding parametrization of transition and noble metal clusters" Int. J. Quantum Chem. 97, 654 (2004)

[2] Aprà E., Carter E. A., Fortunelli A. "On the separability between valence and conduction

bands in transition metal clusters" Int. J. Quantum Chem., 100, 277 (2004)
[3] Aprà E., Baletto F., Ferrando R., Fortunelli A. "Amorphization mechanism of icosahedral metal nanoclusters" Phys. Rev. Lett., 93, 065502 (2004)
[4] Rossi G., Rapallo A., Mottet C., Baletto F., Fortunelli A., Ferrando R. "Magic polyicosahedral core-shell nanoclusters" Phys. Rev. Lett., 93, 105503 (2004)
[5] Henry C. et al. "Nucleation and growth kinetics of gold nanoparticles on MgO(100) studied by UHV-AFM" Appl. Surf. Sci. 226, 167 (2004)
[6] Renaud G., Henry C. et al., "Quantitative analysis of grazing incidence small-angle x-ray scattering: Pd/MgO(001) growth", Phys. Rev. B 69, 035411 (2004)
[7] Rapallo A., Rossi G., Ferrando R., Fortunelli A., Curley B. C., Lloyd L. D., Tarbuck G. M., Johnston R. L. "Global optimization of bimetallic cluster structures. I. Size-mismatched Ag-Cu, Ag-Ni, and Au-Cu systems" J. Chem. Phys., 122, 194308 (2005)
[8] Rapallo A., Rossi G., Ferrando R., Fortunelli A., Curley B. C., Lloyd L. D., Johnston R. L. "Global optimization of bimetallic cluster structures. II. Size-matched Ag-Pd, Ag-Au, and Pd-Pt systems" J. Chem. Phys., 122, 194309 (2005)
[9] Barcaro G., Fortunelli A. "The interaction of coinage metal clusters with the MgO(100) surface" J. Chem. Theor. Comput., 1, 972 (2005)
[10] Ferrando R., Fortunelli A., Rossi G. "Quantum effects on the structure of pure and binary metal nanoclusters" Phys. Rev. B, 72, 085449 (2005)
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[12] Barcaro G., Fortunelli A., Nita F., Ferrando R. "Diffusion of palladium clusters on magnesium oxide" Phys. Rev. Lett., 95, 246103 (2005)
[13] C. Mottet, Rossi G., F. Baletto, Ferrando R., "Single impurity effect on the melting of nanoclusters" Phys. Rev. Lett., 95, 035501 (2005)
[14] Jedrecy, N., G. Renaud, R. Lazzari and J. Jupille. "Flat-top silver nanocrystals on the two polar faces of ZnO : an all angle x-ray scattering investigation." Physical Review B **72**: 045430. (2005)
[15] Jedrecy, N., G. Renaud, R. Lazzari and J. Jupille. "Unstrained islands with interface coincidence sites versus strained islands : X-ray measurements on Ag/ZnO." Physical Review B 72: 195404. (2005)
[16] Revenant, C., G. Renaud, R. Lazzari and J. Jupille. "Growth of Ag on MgO(001) studied in situ by grazing incidence small angle Xray scattering." Nuclear Instruments and Methods in Physics Research B. (2005)
[17] Renaud, G. "Real-time monitoring of growing nanoparticles by in situ small angle grazing incidence X-ray scattering." AIP conference Proceedings 748: 63-72. (2005)
[18] Leroy, F., G. Renaud, A. Letoublon, R. Lazzari, C. Mottet and J. Goniakowski. "Self-organized growth of nanoparticles on a surface patterned by a buried dislocation network." Physical Review Letters **95**: 185501. (2005)
[19] Tusche, C., H. L. Meyerheim, N. Jedrecy, G. Renaud, A. Ernst, J. Henk, P. Bruno and J. Kirschner. "Oxygen induced symmetrization and structural coherency of Fe/MgO/Fe(001) magnetic tunnel junctions." Physical Review Letters 95: 176101. (2005)
[20] O. Meerson, G. Sitja, C.R. Henry, "Low temperature and low pressure CO oxidation on gold clusters supported on MgO(100)", Eur. Phys. J. D, 34, 119 (2005)
[21] C. Barth, C. Claeys, C.R. Henry, "Surface preparation of hard ionic crystals by UHV cleavage", Rev. Sci. Intrum., 76, 083907 (2005)
[22] C.R. Henry, "Morphology of supported nanoparticles", Prog. Surf. Sci., 80, 92 (2005)
[23] E. Aprà, R. Ferrando and A. Fortunelli, "Density-functional global optimization of gold nanoclusters", Phys. Rev. B 73, 205414 (2006)
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[26] L. O. Paz-Borbon, R. L. Johnston, G. Barcaro, A. Fortunelli, "Cross-over among structural motifs in 38-atom binary metal clusters", in preparation
[27] L. O. Paz-Borbon, T. V. Mortimer-Jones, R. L. Johnston, A. Posada-Amarillas, G. Barcaro, A. Fortunelli, "Structure and energetics of 98-atom Pd-Pt nanoalloys: potential stability of the Leary tetrahedron for bimetallic nanoparticles", submitted
[28] G. Barcaro, A. Fortunelli, "Structure and Diffusion of Small Ag and Au Clusters on the Regular MgO(100) Surface", *New J. Phys.*, 9, 22, 1 – 17 (2007)
[29] G. Barcaro, A. Fortunelli, G. Rossi, F. Nita, R. Ferrando, "Epitaxy, Truncations, and Overhangs in Palladium Nanoclusters Adsorbed on MgO(001)", *Phys. Rev. Lett.*, 98, 156101 (2007)
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[31] G. Barcaro, M. Causà, A. Fortunelli, "A comparison between the Absorption Properties of the Regular and F_s-defected MgO(100) Surface", *Theor. Chem. Acc.*, in press (2007)
[32] G. Barcaro, E. Aprà, A. Fortunelli, "Structure of Ag Clusters Grown on the F_s-defected MgO(100) Surface", *Chem. Eur. J.*, in press (2007)
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[34] G. Barcaro, F. Sedona, A. Fortunelli, G. Granozzi, "The Structure of a TiO_x zigzag-like monolayer on Pt(111)", *J. Phys. Chem. C.*, 111, 6095-6102 (2007)
[35] G. Barcaro, F. Sedona, A. Fortunelli, G. Granozzi, "The Structure of TiO_x kagomé-like and wagon-wheel-like monolayers on Pt(111)", in preparation
[36] G. Barcaro, F. Sedona, P. Finetti, A. Fortunelli, G. Granozzi, "UV and XAS analysis of monolayer TiO_x phases on Pt(111)", in preparation
[37] G. Rossi and R. Ferrando, "Global optimization by excitable walkers", Chem. Phys. Lett. 423, 17 (2006)
[38] G. Rossi, C. Mottet, F. Nita and R. Ferrando, " Global Optimization Study of Small ($10 < N < 120$) Pd Clusters Supported on MgO(100)", J. Phys. Chem. B 110, 7436 (2006).
[39] T. J. Toai, G. Rossi and R. Ferrando, "Growth simulations of AuCu nanoalloys", Faraday Discussions, in press (2007)
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[42] A. Videcoq, M. Han, P. Abelard, C. Pagnoux, F. Rossignol and R. Ferrando, "Influence of the potential range on the aggregation of colloidal particles", Physica A 374, 507 (2007)
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[49] Hamm G., Barth C., Wandelt K, Henry CR, "Surface structure of an ultrathin alumina film on Ni3Al(111): A dynamic scanning force microscopy study ", Phys. Rev. Lett., 97, 126106 (2006)
[50] Hamm G., Becker C, Henry CR, "Bimetallic Pd-Au nanocluster arrays grown on nanostructured alumina templates", Nanotechnology, 17, 1943 (2006)
[51] Barth C, Pakarinen OH, Foster AS, Henry CR, "Imaging nanoclusters in the constant height mode of the dynamic SFM", Nanotechnology, 17, S128 (2006)
[52] Barth C, Henry CR, "Kelvin probe force microscopy on surfaces of UHV cleaved ionic crystals", Nanotechnology, 17, S155 (2006)
[53] Hamm G, Marsault M, Wörz A, Sitja G, Henry CR; "Preparation of regular arrays of bimetallic clusters with independent control of size and chemical composition", Faraday Discussion, submitted (2007)
[54] Henry C R, Renaud G et al., "Watching metal cluster growth on an ultrathin alumina film on Ni3Al(111)", in preparation
[55] Barcaro G and Fortunelli A, "A study of metal clusters adsorbed on a double-vacancy-defected MgO(100) terrace", Faraday Discussion, submitted (2007)

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

A figure from ref. [4] in 1A,B has been selected as cover of Phys. Rev. Lett. in September 2004; ref. [4] has also been the subject of an article on PhysWeb (physicsweb.org/article/news/8/9/4/1) and has received appreciable attention in Italian newspapers: "Repubblica", "Il Piccolo" "Gazzetta di Parma", "Unione Sarda", "Metro"). It has a link in the Web site of "Le Scienze" (Italian edition of the "Scientific American") and formed the basis for an article on the same magazine, title: "Magici Nanocluster" by F. Baletto and R. Ferrando, on May 2005. A description of this work has been included into the project Web site.
As for dissemination, the SSA-TMN publications have received good attention within the scientific community. As the latest example, the editor just informed us that the article [28] has been downloaded 250 times in its first three months.

1 D. Patents and industry collaborations

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

The following networking meetings have been held as general project meetings or taking advantage of international conferences to which several SSA-TMN partners took part:

- *SSA-TMN meeting*, Pisa, October 2004
- *Fourth International Workshop on Oxide Surfaces (IWOX4)*, Aussois, France, January 2005
- *Workshop on Surface Nanopatterning*, Pisa, June – July 2005

- *SSA-TMN meeting*, Pisa, October 2005
- *Self-Organized NanoStructures (SONS) – Conference*, Pisa, June – July 2006
- *Summer School on Metal Clusters and Surfaces*, Pisa, July 2006
- *SSA-TMN meeting*, Berlin, October 2006
- *Fifth International Workshop on Oxide Surfaces (IWOX5)*, Lake Tahoe, CA, January 2007

Exchange visits of PhD students or post-docs among different units have been organized to provide an exchange of expertise within the project: G. Barcaro from IP1 to IP2; G. Rossi from IP2 to IP1; F. Leroy from IP3 to AP1.

1 F. Participation in other conferences

Please list only the most relevant

Barcaro G., Fortunelli A., "The interaction of coinage metal clusters with the MgO(100) surface", *MMD Meeting*, Genova, June 22th-25th 2005 .

Barcaro G., Fortunelli A., "Diffusion of palladium clusters on magnesium oxide", *Workshop on Surface Nanopatterning*, Tirrenia (Pisa), June 30, July 1st 2005

Olivier S., Fortunelli A., "A novel Au-Au interaction potential including directionality effects", *Workshop on Surface Nanopatterning*, Tirrenia (Pisa), June 30, July 1st 2005

Barcaro G., Fortunelli A., "DFT study of the interaction of small coinage metal clusters and extended depositions with the regular and defected MgO(100) surface" *Summer School on Self-Organised Nanostructures*, Cargese (Corsica), July 17th-23th 2005

Barcaro G., Fortunelli A., "Metal-oxide potentials: the Pd-MgO case study", *CECAM Workshop on Ab Initio Meets Classical Simulations: The Development of Empirical Potentials for Atomistics Systems*, Lion (France), October 17th-19th 2005

F. Nita G. Rossi, R. Ferrando, C. Mottet, G. Barcaro, A. Fortunelli, Structure and diffusion of Pd clusters on the MgO(001), *23rd European Conference on Surface Science (ECOSS23)*, Berlin September 4-9 2005

Leroy, F., G. Renaud, A. Letoublon, R. Lazzari, T. Schulli, S. Rohart, Y. Girard and Y. Garreau. Self-organized growth of cobalt nano-dots studied in situ by combined grazing incidence X-ray diffraction and small angle scattering. *Symposium on surface science*, Les Arcs (France).(2005)

Renaud, G. X-ray reflectivity and grazing incidence small angle X-ray scattering. *European school on Magnetism : "New experimental approaches in magnetism"*, Constantza (Roumanie).(2005)

Renaud, G., R. Lazzari, N. Jedrecy, C. Revenant and F. Leroy. In situ investigations of growing metal clusters on oxide surfaces by grazing incidence small and wide angle X-ray scattering. The *Fourth International Workshop on Oxide Surfaces*, Aussois (France).(2005)

Renaud, G., F. Leroy, R. Lazzari, A. Letoublon, T. Schülli, S. Rohart, Y. Girard, C. Revenant and M. Ducruet. Growing nanostructures studied in situ by combined grazing incidence small and wide angle scattering. *XIII congress of the "Societa Italiana di Luce di Sincortrone"*, Modena (Italie).(2005)

Renaud, G., F. Leroy, A. Letoublon, R. Lazzari, T. Schülli, S. Rohart, Y. Girard and Y. Garreau. Self-organized growth of cobalt nano-dots studied in situ by combined grazing incidence X-ray diffraction and small angle scattering. *Nanopatterning at surface, workshop of the SONS*, Pisa (Italie).(2005)

Revenant, C., G. Renaud, R. Lazzari and J. Jupille. Growth of Ag on MgO(001) studied in situ by grazing incidence small angle Xray scattering. *European – Material Research Society 2005*, Strasbourg (France).(2005)

IWTF2 Conference, Prague (Czech Republic) June 26-30 2006 invited oral presentation - R. Ferrando, "Structure, diffusion and growth of Pd clusters on MgO(001)".

Summer School on metal clusters and surfaces, Tirrenia (Pisa) July 3-6 2006, 3 lectures - R.

Ferrando "Simulations of the growth and dynamics of metal clusters and surfaces".

ISSPIC 13 Conference, Goteborg, 24-28 July 2006, two poster presentations - G. Rossi and R. Ferrando, "Global optimization by excitable walkers" - G. Barcaro, A. Fortunelli, G.Rossi, F. Nita and R. Ferrando, "Electronic and geometric effects in AgCu and AuCu nanoclusters"

233rd ACS National Meeting, Chicago (USA), March 25-29 2007 Invited plenary lecture in the session Nanoscale Inorganic Catalysis - R. Ferrando "Structure and growth of alloy nanoclusters"

Summer School on metal clusters and surfaces, Tirrenia (Pisa) July 3-6 2006, 3 lectures - C. R. Henry " Metal deposition on oxide surfaces". Summer School on metal clusters and surfaces, Tirrenia (Pisa) July 3-6 2006, 3 lectures - F. Leroy " GISAXS studies of surface growth and patterning".

Barth C, Hamm G, HENRY CR, “Surface structure of nanostructured ultrathin alumina films” and “Self organized growth of bimetallic clusters on a nanostructured alumina surface”, Self-Organized Nanostructures, SONS2006, Pisa (Italy), July 2006 (invited talk)

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

G. Barcaro, PhD, 30/09/2003-15/04/2007: PhD achieved on February 15th 2007
S. Olivier, post-doc, 01/09/2004-30/09/2004 + 01/03/2006-31/03/2006
F. Nita, post-doc, 01/06/2004-15/04/2007
Exchange visits from other groups: Prof. R. L. Johnston, L. O. Paz, M. Alcantara-Ortigoza.

EUROPEAN SCIENCE FOUNDATION	**EUROCORES Programme** European Collaborative Research **SONS** **Self-Organized NanoStructures**

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (): Acronym / Short Title: SONS-NANOSYN Full Title: Project Leader name: Project Leader affiliation: Institutional home page (URL): Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1 …
Principal Investigator (name & affiliation):
Total Funding amount of the IP *(to be corrected by the PI)*
AP 1
Principal Investigator (name & affiliation):

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The most important achievement of our CRP is the interaction which has been created between the persons working in the fields of physics and chemistry with the common goal to show scientific progress in the field of molecular electronics. We learnt much from each other while focusing on common targets and also during many common workshops both communities met for discussions and planning for our joint research work. The synthetically focused research groups prepared many target compounds which then were investigated by physical methods.

These methods were set for the fabrication and characterization of molecular junctions down to the level of single molecules. We have demonstrated and characterized atomic contacts from break junctions operated at room temperature and in liquid environment.

Although a variety of promising results in such systems are available in the literature, our still limited insight in the microscopic details of molecular junctions is reflected by the large discrepancies reported for the conductance of single molecule junctions. Of foremost relevance to this problem is the data analysis scheme applied to transport measurements. We have devised a new, robust analysis based on simple tunneling physics and demonstrated its efficiency for alkanedithiol junctions. This study has set a firm basis to pursue with the investigation of conjugated phenylene derivatives.

For substrates with limited flexibility such as glass, electromigration represents an interesting alternative for the fabrication of nanometer-scale gaps in metallic electrodes. We have developed and implemented a four-terminal junction geometry combined with hardware feedback electronics to improve the control of the electromigration process in Au nanowires.

An additional approach for the parallel fabrication of molecular junctions based on the stamping of alkanethiol-coated colloid arrays has been successfully implemented. Conjugated phenylene derivatives were inserted within the 2D arrays via a place-exchange reaction. Remarkably, the transport measurements performed on structures involving typically 106 junctions provided single molecule conductance values in excellent agreement with the break junction approach. Finally, a complementary technique was developed, based on the dielectrophoretic trapping of colloidal particles. There, the controlled assembly of 1D chains of colloids was demonstrated.

Molecular junctions conductance: To account for junction-to-junction fluctuations, the variation of conductance during the formation of a metal-molecule-metal junction is measured for a large number of successive breaking processes (typically 100 here), as illustrated in Fig. 1. Conductance histograms are then built from the conductance traces G(z) acquired, an analysis first implemented for atomic contacts. Peaks in the histogram point to preferred junction geometries. Evidence for the formation of few-molecules junctions was derived from the observation of satellite peaks appearing at multiples of a fundamental conductance value, attributed to a single-molecule junction. So far, the histograms were built from selected conductance traces for the analysis of molecular junctions. This represents a quite unsatisfactory situation since such a process is always prone to some degree of subjectivity. We proposed a new analysis scheme and could demonstrate its validity for a model system: octanedithiol (C8) junctions.

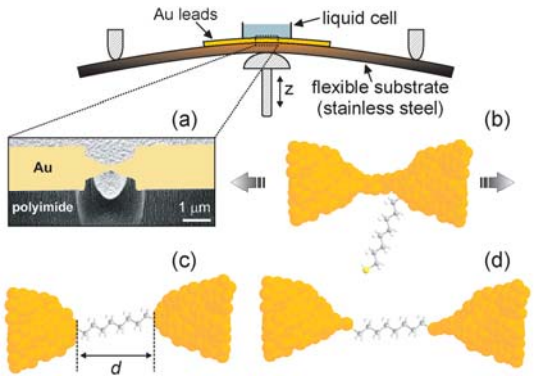


Fig. 1: (a) Schematics of the MCBJ principle with a SEM image of microfabricated Au bridge. **(b-d)** Starting the breaking process from the closed Au bridge (b), a octanedithiol molecule can then lock between the leads (c). Further stretching deforms the Au leads while the molecule remains bound to the Au (d) until it finally breaks off.

Conjugated wires:
Based on our developed understanding of alkanedithiol junctions, we performed a systematic study of thiolated oligo(phenylene ethynylene) (OPE) compounds. These compounds were also addressed in molecular junctions networks prepared from in colloid arrays. The complementarity of the two approaches is a unique opportunity to gain a deeper insight in the electrical properties of molecular junctions.

First results are shown in Fig. 2, where four conductance histograms are represented for four distinct conjugated compounds. The conductance histograms were built from 100 consecutive conductance traces recorded during the breaking of the Au bridge in presence of a 0.1mM solution. The histograms are shown after substracting the tunneling background, following the procedure described above. The white-dashed lines emphasize the different peaks observed as obtained from a multiple-

peak fit of the histograms. The peak corresponding to a single-molecule junction is found at a conductance value of $G_{1,OPV} \approx 2.2 \cdot 10^{-4}$ G_0 for the phenylene vinylene compound (OPV) and $G_{1,OPE} \approx 1.1 \cdot 10^{-4}$ G_0 for the phenylene ethynylene (OPE) molecule. We interpret the satellite peaks as a signature for the formation of parallel molecular bridges. Clearly, we observe a slightly higher conductance for the OPV compound. This points towards a better π-orbital overlap for this compound. The presence of side groups (-OCH_3 and –OC_6H_{13}) improving the solubility of the OPE compound does not significantly alter the conductance measured. Remarkably enough, we find similar conductance values for this compound in colloid arrays. Recent findings in STM break junctions confirm this value as well. Finally, we note that the width of the conductance peaks is substantially larger for the OPE and OPV compounds than for the octanedithiols. We speculate that this is due to the larger rigidity (and length) of the OPE molecule as compared to that of the alkane chain. Additional investigations to address this specific aspect are under way.

With these measurements, we confirm the validity of our background substraction procedure for the analysis of the conductance histograms in the case of conjugated molecules. We expect that, by inducing slight structural variations in the molecular structure (additional side groups, different anchor terminals), we will gain additional insight into the effects of microscopic conformational changes on the conductance properties of molecular junctions.

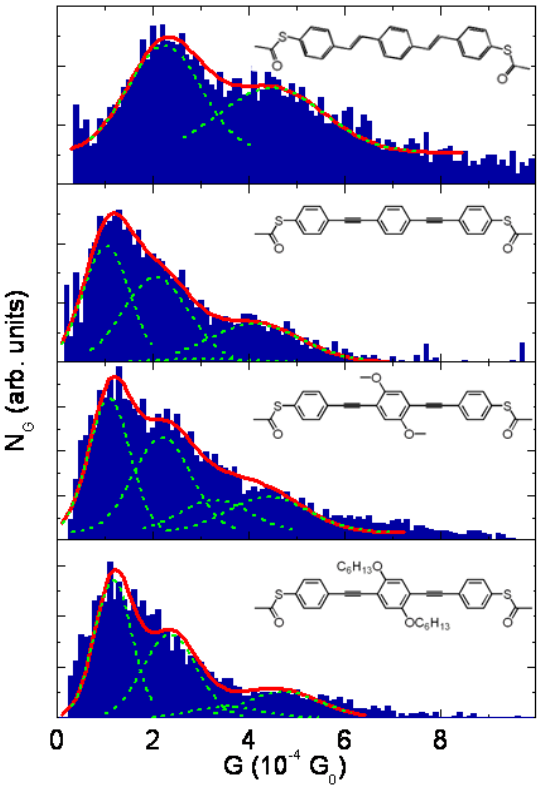


Fig. 2: Conductance histograms, after subtraction of the tunneling background, for a 0.1mM solution of various thiolated OPE molecules. Red curves: sum of the dashed Gaussian curves obtained from a multiple peak fit.

With this short out-line we show that there is a real need in a detail study of fundamental issues dealing with the field of molecular electronics. There is only a chance for scientific progress in this area when chemists and physicists work closely together – and that's the real achievement of this programme.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

There is no major deviation from the overall plan. This does not mean that in detail, for instance, all the compounds listed in the plan could be synthesized and tested, but that is inherent to scientific projects; if a scientific plan is fulfilled in detail – it would not match with research at the forefront of science.
Our main target, namely to bring the disciplines of physics and chemistry together to work on common scientific goals, could be fully and successfully reached.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

This CRP SONS-NANOSYN nucleated and initiated the submission of two new projects:

a) An ITN within FP7 with the title: “Fundamentals of Molecular Electronic Assemblies”. The aim is to combine expertise in synthetic chemistry, nanoscale physics and device engineering, surface electrochemistry and high-level electronic structure calculations.

b) A RNP research proposal on the topic of molecular electronics.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

Our recommendations are to continue on similar / analogous topics which refer to the molecular (nano) scale of any kind of assemblies; programmes like SONS are very successful in our opinion and should not be changed much for a longer time period - science at the forefront needs continuation and not too many changes;
it is really important to note that this programme allowed very successfully the collaborations across disciplines, mainly physics, biology and chemistry.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

It is a very good programme across disciplines – with a very good support from the ESF office – it gives means to conduct research, to meet, to discuss, to move forward in science, and not as it is the case in other programmes, mainly to manage science for any goal of integration;
The ESF programmes are much better arranged for science then the heavily administrative FP6 (FP7) programmes from Bruxell - being involved on both sides, we can clearly distinguish them – good to know that we have ESF programmes in Europe.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The ESF programmes are on a good track since long. The procedures are good and do not need major changes.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

1. Exceptionally Small Attenuation Factors in Molecular Wires. F. Giacalone, J.L. Segura, N. Martín, D.M. Guldi. *J. Am. Chem. Soc.* **2004**, *126*, 5340.

2. Electronic communication through π-conjugated wires in covalently linked porphyrin/C_{60} ensembles. G. de la Torre, F. Giacalone, J.L. Segura, N. Martín, J. Ramey, D.M. Guldi. *Chem. Eur. J.* **2005**, *11*, 1267.

3. Probing Molecular Wires: Synthesis, Structural, and Electronic Study of Donor–Acceptor Assemblies Exhibiting Long-Range Electron Transfer. F. Giacalone, J.L. Segura, N. Martín, J. Ramey, D. M. Guldi. *Chem. Eur. J.* **2005**, *11*, 4819.

4. Connecting two C_{60} stoppers to molecular wires: ultrafast intramolecular deactivation reactions. C. Atienza, B. Insuasty, C. Seoane, N. Martín, J. Ramey, G. M. Aminur Rahman, D. M. Guldi. *J. Mater.Chem.* **2005**, *15*, 125.

5. Tunning Electrón Transfer through p-Phenyleneethynylene Molecular Wires. C. Atienza, N. Martín, M. Wielopolski, N. Haworth, T.Clark, D.M. Guldi. *Chem. Commun.***2006**, 3202.

6. Electronic Interactions in a New π-Extended Tetrathiafulvalene Dimer. M. C. Díaz, B. M. Illescas, N. Martín, I. F. Perepichka, M. R. Bryce, E. Levillain, R. Viruela, E. Ortí. *Chem. Eur. J.* **2006**, *12*, 2709.

7. Energy versus Electron Transfer in Oligofluorene-C_{60} and C_{60}-Oligofluorene-C_{60} Donor-Acceptor Cpnjugates. C. van der Pool, M.R. Bryce, D. M. Guldi, S. Filippone, N. Martín. *J. Org. Chem.*, submitted.

8. Tetrathiafulvalene-based molecular electrical wires. F. Giacalone, M. A. Herranz, L. Güter, M. T. González, M. Calame, C. Schönenberger, N. Martín, in preparation.

- R. Huber, M. T. Gonzalez, S. Wu, V. Horoiu, M. Mayor, M. Bryce, C. Schönenberger, and M. Calame. ***Conductance comparison of conjugated molecules in liquid environment***, in preparation.

M. Haas, S.-X. Liu, A. Kahnt, C. Leiggener, D. M. Guldi, A. Hauser and S. Decurtins; *J. Org. Chem.*, 2007, submitted.

Photoinduced Energy Transfer Processes within Dyads of Metallophthalocyanines Compactly Fused to a Ruthenium(II) Polypyridine Chromophore.

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

[1] Lithiation of a Pyrrolo Annulated Tetrathiafulvalene
B. M. Petersen, J. O. Jeppesen,* J. Becher
Synthesis **2004**, 2555–2559.

[2] Complete Sequential Functionalization of Monopyrrolo-Tetrathiafulvalenes
H. Gopee, K. A. Nielsen, J. O. Jeppesen*
Synthesis **2005**, 1251–1260.

[3] 4,5-Bis(hydroxymethyl)-1,3-dithiole-2-thione
J. M. Pløger, B. M. Petersen, A. D. Bond, J. O. Jeppesen *
Acta Cryst. **2006**, E62, o2066–o2068.

[4] Characterization of a Byproduct in the Alkylation of DMIT: Alkylation on the Least Nucleophilic Sulfur Atom
B. M. Petersen, J. K. Bjernemose, J. O. Jeppesen*
Eur. J. Inorg. Chem. **2006**, 3099–3104

[5] Supramolecular Receptor Design – Anion-Triggered Binding of C_{60}
K. A. Nielsen, W.-S. Cho, G. Sarova, B. M. Petersen, A. D. Bond, J. Becher, F. Jensen, D. M. Guldi, J. L. Sessler,* J. O. Jeppesen*
Angew. Chem. Int. Ed. **2006**, *45*, 6848–6853.

[6] A bromine catalyzed dimerization of α,α′-bishalomonopyrrolo-TTFs
H. Gopee, B. M. Petersen, A. D. Bond, J. O. Jeppesen*
Chem. Commun. **2007**, in preparation.

1. Largely p-Quinonoid π–Extended Tetrathiafulvalene Derivatives: A Class of Highly Distorted Electron Donors. M.C. Díaz, B.M. Illescas, N. Martín, R. Viruela, P.M. Viruela, E. Ortí, O. Brede, I. Zilbermann, D.M. Guldi. *Chem. Eur. J.* **2004**, *10*, 2067.

2. Synthesis and electron donor ability of the first conjugated π-extended tetrathiafulvalene (exTTF) dimmers. M.C. Díaz, B.M. Illescas, C. Seoane, N. Martín. *J. Org. Chem.* **2004**, *69*, 4492.

3. Mimicking photosynthesis: covalent [60]fullerene-based donor-acceptor ensembles. N. Martín, F. Giacalone, J.L. Segura, D.M. Guldi. *Synth. Met.* **2004**, *147*, 57.

4. Hydrogen-Bonding Motifs – Implementation of this remarkable functionality into Fullerene chemistry. L. Sánchez, N. Martín, D.M. Guldi. *Angew. Chem. Int. Ed.* **2005**, *40*, 1372.

5. Materials for Organic Solar Cells: the C_{60}/π-conjugated Oligomer Approach. J.L. Segura, N. Martín, D.M. Guldi. *Chem. Soc. Rev.* **2005**, 31.

6. Solid film versus solution phase charge recombination dynamics of exTTF-bridge-C_{60} dyads. S. Handa, F. Giacalone, S. A. Haque, E. Palomares, N. Martín, J. R. Durrant. *Chem. Eur. J.* **2005**, *11*, 7440.

7. Topological Effects of a Rigid Charal Spacer on the Electronic Interactions in Donor-Acceptor Ensembles. D.M. Guldi, F. Giacalone, G. de la Torre, J.L. Segura, N. Martín. *Chem. Eur. J.* **2005**, *11*, 7199.

8. C_{60}-based dumbbells: connecting C60 cages through electroactive bridges. L. Sánchez, M.A. Herranz, N. Martín. *J. Mater. Chem.* **2005**, *15*, 1409.

9. Highly Efficient Light-Harvesting Organofullerenes. R. Gómez, J.L. Segura, N. Martín. *Org. Lett.* **2005**, *7*, 717.

10. C_{60}-exTTF-C_{60} Dumbbells: Cooperative Effects Stemming from Two C_{60}s on the Radical Ion Pair Stabilization. L. Sanchez, M. Sierra, N. Martín, D.M. Guldi, M.W. Wienk, R.J.A. Janssen. *Org. Lett.* **2005**, 7, 1691.

11. Efficient Electron Transfer in Tetrathiafulvalene Modified Single-Walled Carbon

Nanotubes. M.A. Herranz, N. Martín, S. Campidelli, M. Prato, G. Brehm, D.M. Guldi. *Angew. Chem. Int. Ed.* **2006**, *45*, 4478.

12. Sinergy of H-bonding and Electrostatic Interactions for improving the Electronic Communication in Donor-Acceptor Ensembles. L. Sánchez, M. Sierra, N. Martín, A. J. Milles, T. J. Dale, J.S. Rebeck, W. Seitz, D.M. Guldi. *Angew. Chem. Int. Ed.* **2006**, *45*, 4637.

13. New Challenges in Fullerene Chemistry. N. Martín. *Chem. Commun.* **2006**, 2093.

14. Electron Aceptor Fullerenes. B. M. Illescas, N. Martín. *Comptes Rendues de Chimie* **2006**, 1038.

15. exTTF as a Building Block for Fullerene Receptors. Unexpected Solvent-Dependent Positive Homotropic Cooperativity. E. M. Pérez, L. Sánchez, G. Fernández, N. Martín. *J. Am. Chem. Soc.* **2006**, *128*, 7172.

16. Self-Assembly of C_{60} π-Extended Tetrathiafulvalene (exTTF) Dyads on Gold Surfaces. M. Sierra, M. A. Herranz, S. Zhang, L. Sánchez, N. Martín, L. Echegoyen. *Langmuir* **2006**, *22*, 10619.

17. Molecular Panels for Energy Transduction in C_{60}-Based Conjugates. L. Sánchez, N. Martín, E. González-Cantalapiedra, A. M. Echavarren, G. M. Aminur Rahman, D. M. Guldi. *Org. Lett.* **2006**, *8*, 2451.

18. Supramolecular pseudorotaxane type complexes from π-extended TTF dimer crown ether and C_{60}. M. C. Díaz, B. M. Illescas, N. Martín, J. F. Stoddart, M.A. Canales, J. Jiménez-Berbero, G. Sarova, D. M. Guldi. *Tetrahedron* **2006**, *62*, 1998.

19. Concave TTF-type Donors as Supramolecular Partners for Fullerenes. E. M. Pérez, M. Sierra, L. Sánchez, M. R. Torres, R. Viruela, P. M. Viruela, E. Ortí, N. Martín. *Angew. Chem. Int. Ed.* **2007**, 46, 1847.

20. Electron Transfer in Me-blocked Heterodimeric α,γ-Peptide Nanotubular Donor-Acceptor Hybrids. R. J. Brea, L. Castedo, J. R. Granja, M. A. Herranz, L. Sánchez, N. Martín, W. Seitz, D.M. Guldi. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 5291.

- M. T. Gonzalez, S. Wu, R. Huber, S.J. Molen, C. Schönenberger, and M. Calame. ***Electrical conductance of molecular junctions by a robust statistical analysis***. Nano Lett., **6**, 2238 (2006).
- J. Liao, L. Bernard, M. Langer, C. Schönenberger, and M. Calame, ***Reversible formation of molecular junctions in two-dimensional nanoparticle arrays***, Adv. Mat. **18**(8), 2444 (2006); Cited by L. Venemaa, Nature, News&Views, August 31st 2006.
- M. Calame and C. Schönenberger. ***Molecular electronics***, Imaging & Microscopy, **8**,36, June 2006.
- C. Schönenberger and M. Calame. ***Building break junctions for molecular electronic***s, NanoNews, Newsletter of the NCCR Nanoscale Science, p26, January 2006.
- C. Schönenberger, M. Calame, and M. Mayor. ***Schaltende Moleküle***, UniNova, Wissenschafts-magazin der Universität Basel, **103**, 22, July 2006.
- Laetitia Bernard, ***Expanding the Horizon of Molecular Electronics via Nanoparticle Assemblies***, PhD thesis, Department of Physics, University of Basel, Basel, Sept. 2006.

- C. Jia, S.-X. Liu, C. Tanner, C. Leiggener, E. Levillain, S. Leutwyler, A. Hauser, S. Decurtins, *Chem. Commun.* **2006**, 1878.
  A Redox-Active Tri-Star Molecule: Merging of TTF and HAT Chemistry.
- C. Jia, S.-X. Liu, C. Ambrus, A. Neels, G. Labat, S. Decurtins, *Inorg. Chem.* **2006**, *45*, 3152.
  A One-Dimensional μ-Chloro-Mn(II)-Tetrathiafulvalene (TTF) Coordination Compound.
- S.-X. Liu, C. Ambrus, S. Dolder, A. Neels, S. Decurtins, *Inorg. Chem.* **2006**, *45*, 9622.
  A Dinuclear Ni(II) Complex with Two Types of Intramolecular Magnetic Couplings: Ni(II) – Ni(II) and Ni(II) – $TTF^{\bullet+}$.
- C. Jia, S.-X. Liu, C. Tanner, C. Leiggener, A. Neels, L. Sanguinet, E. Levillain, S. Leutwyler, A. Hauser, S. Decurtins, *Chem. Eur. J.* **2007**, *13*, 3804.

An Experimental and Computational Study on Intramolecular Charge Transfer: A Tetrathiafulvalene-Fused Dipyridophenazine Molecule.

- C. Goze, C. Leiggener, S.-X. Liu, L. Sanguinet, E. Levillain, A. Hauser, S. Decurtins, *ChemPhysChem.* **2007**, in press.
  Fused Donor-Acceptor Ligands in Ru(II) Chemistry: Synthesis, Electrochemistry and Spectroscopy of $[Ru(bpy)_{3-n}(TTF\text{-}dppz)_n](PF_6)_2$ (n = 1-3, TTF-dppz = 4',5'-bis(propylthio)tetrathiafulvenyl[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine).

1. C. van der Pol, M. R. Bryce, M. Wielopolski, C. Atienza-Castellanos, D. M. Guldi, S. Filippone, N. Martín, Energy vs Electron Transfer in Oligofluorene-C60 and C60-Oligofluorene-C60 Conjugates, *J. Org. Chem*., accepted (May 2007) subject to revisions.

2. D. M. Guldi, F. Späning, D. Kreher, I. F. Perepichka, C. Van der Pol, M. R. Bryce, K. Ohkubo, and S. Fukuzumi , Contrasting Photodynamics between C_{60}–dithiapyrene and C_{60}–pyrene Dyads, *Chem. Eur. J*. to be submitted May 2007.

3. S. Amriou, I. F. Perepichka, A. S. Batsanov, M. R. Bryce, C. Rovira, J.Vidal-Gancedo, Remarkable Interplay of Redox States and Conformational Change in a Sterically Crowded Cross-Conjugated Tetrathiafulvalene Vinylog, *Chem. Eur. J.*, **2006**, *12*, 5481-5494.

4. M. C. Díaz, B. M. Illescas, N. Martín, I. F. Perepichka, M. R. Bryce, E. Levillain, R. Viruela, E. Ortí, Electronic Interactions in a New π-Extended Tetrathiafulvalene Dimer, *Chem Eur. J.*, **2006**, *12*, 2709-2721.

5. F. B. Dias, S. Pollock, G. Hedley, L.-O. Pålsson, A. Monkman, I. I. Perepichka, I. F. Perepichka, M. Tavasli, M. R. Bryce, Fast Intramolecular Charge Transfer assisted by Conformational Changes in the Excited State of Fluorene-Dibenzothiophene-*S*,*S*-dioxide Oligomers. *J. Phys. Chem. B*, **2006**, *110*, 19329-19339.

6. I. I. Perepichka, I. F. Perepichka, M. R. Bryce, L.-O. Pålsson, Dibenzothiophene-*S*,*S*-dioxide – fluorene co-oligomers. Stable, highly-efficient blue emitters with improved electron affinity. *Chem. Commun.*, **2005**, 3397–3399.

Newspaper Articles:

1. La Microtecnología ha muerto ¡Viva la Nanotecnología! N. Martín, *El País*, Future, Wednesday, January 18th, 2006

2. Apagón Químico. N. Martín, P. Espinet, *El País*, Press Box, Wednesday, March 7th, 2007

- B. Peiseler-Sutter, **Chemische Rundschau** 11**,** 56 (2006)

1 D. Patents and industry collaborations

[1] Explosives detection markers
J. O. Jeppesen, Kent A. Nielsen
Danish Patent Application PA 2006 00678

During the CRP close collaboration has developed with QinetiQ (Malvern, UK – contact Dr I. Sage) and IBM Zurich Research Laboratories (Zurich, Switzerland- contact Dr H. Riel).

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

Post-Doc Kent A. Nielsen (Odense University) was a guest scientist in Dirk Guldis (Erlangen) research group in May 2005.

Ph.D. student Bo M. Petersen (Odense University) was a guest ph.d student in Nazario Martins (Madrid) research group from June 06 to December 06.

Research-Assistant Dr. S.-X. Liu (Bern University) was a guest scientist in the Odense-Laboratory, Denmark.

Master student, Leo Heiniger, Bern University, was conducting a research project in Dirk Guldis (Erlangen) research group.

1. NANOSYN meeting in Basel, Switzerland, November 2004. Molecular Wires: Long-Range Electron Tunneling and Hopping in Novel C_{60}-Based Donor-Acceptor Ensembles. N Martín and F. Giacalone. Oral presentation.

2. NANOSYN meeting in Madrid, Spain, September 2005. Electroactive Organic Compounds. M. A. Herranz. Oral presentation.

3. NANOSYN meeting in Durham, UK, September 2006. Tetrathiafulvalene-based molecular electrical wires. F. Giacalone, M. A. Herranz and N. Martín. Oral presentation.

4. NANOSYN meeting in Durham, UK, September 2006. Synthesis of Oligofluorene-C_{60} and C_{60}-Oligofluorene-C_{60} Donor-Acceptor Conjugates. S. Filippone, N. Martín, C. van der Pool, M. Bryce, Oral presentation.

Visits and Secondments of research within the CRP laboratories:

1. Mª Ángeles Herranz, researcher from the Madrid group, visited the Erlangen laboratories (July 2005) to investigate the photophysical properties of SWNT/exTTF nanoconjugates previously synthesized in Madrid.

2. Carmen Atienza, Ph.D. from the Madrid group, carried out her postdoctoral work in the Erlangen group (July 2005-July 2006) working on the photophysical characterization of π-conjugated wires in covalently linked exTTF/C_{60} ensembles

3. Cornelia van der Pol, Ph.D. student from the Durham group, visited the Madrid group to collaborate in the preparation of C_{60}-based molecular wire structures during October 2005.

4. Bo Petersen, Ph.D. student from the Odense group, worked for six months (July-December 2006) in the Madrid group in the construction of C_{60}-oligomer-TTF wires.

- SONS Workshop, Kloster-Irsee, Germany, 16-19 April 2006.
  M.Calame. From single molecules junctions to networks of molecular junctions, talk.

- SONS Workshop Pisa, Italy, 28 Jun-1 Jul 2006.
  R. Huber, S.Wu, M. T. Gonzalez, H. Breitenstein, P. Reinmann, C. Schönenberger, and M. Calame, Break Junctions in liquid for molecular electronics, poster.
  M. T. Gonzalez, Statistical analysis of the electrical conductance of molecular junctions, talk.

- SONS Workshop, Durham, UK, 27-28 Sept 2006.
  M. Calame, Transport in molecular junctions, talk at SONS Workshop, Durham, UK, 26-28 Sept. 2006.

- SONS Workshop, Erlangen, Germany, 28-31 March 2007.

  M. T. Gonzalez, Understanding conductance histograms of single molecular junctions, talk.

1 F. Participation in other conferences

Please list only the most relevant

Jan O. Jeppesen (Odense University) participated in the Seventh International Symposium on Functional π-Electron Systems, Osaka, Japan, May 15–20, 2006.

Besides poster and oral presentations in several national and international (ACS, ECS, ESF, etc..) meetings during these three years, the Madrid group has organized the following conferences:

1. Electrochemical Society Symposium on Molecular and Supramolecular Chemistry of Fullerenes and Carbon Nanotubes, Québec, 2005

2. Electrochemical Society Symposium on Molecular and Supramolecular Chemistry of Fullerenes and Carbon Nanotubes, Denver, 2006

3. International Complutense Seminar on Materials for Renewable Energies, Madrid, 2007

- M. T. Gonzalez, L. Grüter, R. Huber, Z.M. Wu, F. Cheng, T. T. Heikkilä, F. Diederich, M. Calame, and Ch. Schönenberger, *Break Junctions in liquid for molecular electronics*, Talk at the IV Reunion nacional de fısica del estado solido (GEFES), Alicante (Spain), 1.-3. Feb. 2006.
- C. Schönenberger, *Molecular Electronics: from single junctions to networks*, invited talk at the Swiss Physical Society anual meeting at Lausanne, 13-14. Feb. 2006.
- L. Bernard, J. Liao, M. Calame, and C. Schönenberger, *Networks of molecular junctions*, poster at the Swiss Physical Society anual meeting at Lausanne, 13-14. Feb. 2006.
- M. T. Gonzalez, *Break junctions in liquid for molecular electronics*, invited talk at the Spanish Molecular Electronics Symposium, San Sebastian (Spain), 24. March 2006.
- M. Calame, *Paving the road for single molecule electronics*, talk at the Nano-Convention, Scientific Workshop, Bern, 23. June 2006.
- L. Bernard, *Two-dimensional networks of molecular junctions*, talk at the conference “From Solid State

to Biophysics III", Cavtat, Croatia, 24. June – 1. July 2006.

- L. Bernard, *Reversible 2D networks of molecular junctions*, talk at the International Conference of Nanoscience and Technology (ICN+T) 2006, Basel, Switzerland, 31. July – 4. Aug. 2006.
- M. T. Gonzalez, *Interpretation of conductance histograms in single molecular junctions*, talk at the International Conference of Nanoscience and Technology (ICN+T) 2006, Basel, Switzerland, 31. July – 4. Aug. 2006.
- M. Calame, *From single molecule contacting to networks of molecular junctions*, invited talk at the Summer School of the DFG-Center for Functional Nanostructures on 'Molecular Nanostructures' at Bad Herrenalb, 31. Aug. – 2. Sept. 2th 2006.
- M. Calame, *Molecular electronics: From single junctions to networks*, invited talk at the 'Nanomesh Workshop', Braunwald, Switzerland, 17.20. Sept. 2006.
- L. Bernard, *Nanoparticle Assemblies with a View to Molecular Electronics*, talk at "Nanoelectronics Days", Aachen, Germany, 11.-13. Oct. 2006.
- C. Schönenberger. *Molecular Electronics.* Talk at the "Frimat: Cérémonie d'ouverture", Fribourg, Switzerland, 30. Nov. 2006.

Oral presentations by Professor Bryce and/or Dr Perepichka from the CRP were given at:

1. 8th European Conference on Molecular Electronics, ECME8, Bologna, Italy, June 2005.

2. Royal Society of Chemistry Faraday Discussion Meeting "Molecular Wires and Nanoscale Conductors", Manchester, UK, September 2005.

3. 7th International Conference on Functional pi-Electron Systems, Osaka, Japan, May 2006.

4. International Conference on Nanoscience and Technology, ICT+N 2006, Basel, Switzerland, August 2006.

5. Materials Research Society Fall Meeting, Boston, USA, November 2006.

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

Odense:

Hemant Gopee, post doc (01 / December / 2003 to 28 / February / 2005),
100% financed by SONS

Kent A. Nielsen, post doc (01 / December / 2004 to 31 / December / 2004) and
(01 / December / 2005 to 31 / July / 2006)
100% financed by SONS

Bo M. Petersen, Ph.D. student (01 / March / 2004 to 31 / May / 2007),
17% financed by SONS

Madrid:

Dr. Francesco Giacalone

Postdoctoral Research Assistant

Funded from 01/10/2004 to 31/05/2005

Dr. Salvatore Filippone

Postdoctoral Research Assistant

Funded from 01/10/2005 to 31/11/2006

Basel:

Roman Huber, from 1.02.2004 to 31.12.2006
Laetitia Bernard, from 1.01.2005 to 1.01.2007
Teresa Gonzalez, 75% for 7 months in 2006

Bern:

Stefan Dolder, from 01.08.2005 to 30.12.2005

Xavier Guegano, from 01.05.2004 to 30.04.2007

Durham:

Dr Igor F. Perepichka, - 01 February 2004 - 23 March 2007

EUROPEAN SCIENCE FOUNDATION

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (): Acronym / Short Title: SASMEC Full Title: Project Leader name: Project Leader affiliation: Institutional home page (URL): Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1 …
Principal Investigator (name & affiliation):
Total Funding amount of the IP *(to be corrected by the PI)*
AP 1
Principal Investigator (name & affiliation):

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The goal of our CRP was to deepen our understanding of metallic chains of single atoms and single-molecule junctions, by making a very detailed experimental characterization and using state-of-the-art ab initio calculations. Most of the results we have obtained in this CRP (summarized below) required the coordinated interaction of the experimental and theoretical groups in the CRP. The only exception to this are possibly the "Experimental developments" that could have been achieved without the involvement of the CRP.

MAIN SCIENTIFIC ACHIEVEMENTS

1. Mechanical properties of suspended atomic chains. We have studied the mechanical properties of gold atomic chains using direct force measurements and electron-phonon interaction as a probe, and ab initio simulations. We have found that the compliance of sufficiently long chains is additive, that is depends linearly on the number of interatomic bonds, this makes possible to separate the contribution from the electrodes and have direct access to the intrinsic mechanical properties of the chain, and investigate the properties of a single interatomic bond. We have also found that gold atomic chains cannot be compressed, they are always in tensile strain and contract in a peculiar atom by atom process, due to surface energy. The energetics of the process of adding one atom to the chain can be directly measured. The interaction between experimental and theoretical groups have been essential.

2. Electron-phonon interaction in atomic chains and molecular junctions. Vibrational spectroscopy is a powerful tool to analyze the structure of atomic and single-molecule junctions. We have obtained first principles results for phonon signals in IV and the local heating for atomic Au chains, with good agreement with our previously obtained experimental results. Our theory can explain the experimental features: (i) A single main conductance drop is observed, (ii) the order of magnitude of the conductance drop, (iii) the mode softening, and (iv) the increased phonon signal with strain. (v) the frequency shift with strain corresponding to a softening of the bonds in the chain.

Zero-bias anomalies and low voltage features are often observed in nanocontacts and molecular junctions, as well as in atomic chains. We have developed an interpretation of this effect and it appears that it is a promising internal amplification effect for vibration mode spectroscopy.

LOE approximation. Theoretically we have extended the LOE approximation to finite temperatures and verified the accuracy of the LOE by comparing with the full SCBA for atomic wires and molecular wires. This makes possible to do DFT calculations of IETS on relatively large systems in the perturbative limit, for transport ranging from tunneling to contact. Detailed comparison with experiments shows very good agreement.

Simple analytical models. We have also derived simple analytical models for a single site and for an atomic wire connected to contacts provide insights and simple intuitive formulas. For example, these formulas can be used to understand whether the emission of phonons increase or decrease the current through the device. They show that there is a limit on the amount of heat dissipated into the device since the electrons both emit (heat) and absorb (cool) the phonons. They can further be used to fit the experimental data for both atomic gold wires and the hydrogen atom in a platinum break-junction,

revealing relevant physical parameters. Discussions with the experimental groups have been very important.

3. Enhanced atomic chain formation for Au, Ag, and Cu by incorporating oxygen. Stimulated by predictions of one of our theoretical teams, we have performed experiments to investigate the possibility of incorporating oxygen atoms into a metallic chain of gold atoms. We have obtained evidence that in the presence of oxygen atomic chains form to longer lengths and up to higher temperatures, consistent with the predicted enhanced stability of a Au-O chain (the Au-O bond is predicted to be stronger than the Au-Au bond). The conductance remains close to $1G_0$, in agreement with the calculations. Moreover, we discovered that Ag and Cu, which in pure form do not form atomic chains, built chains as long as those for Au when exposed to oxygen. We have evidence that other transition metals may also be induced to form chains.

4. Conductance of simple molecules as benchmark systems.
Pt-H_2-Pt nanocontacts. A hydrogen molecule connected to Pt leads has been fully characterized. Structure and vibrational properties of the system and their variation with strain were determined in a combined experimental and computational investigation. Shot noise measurements showed the conductance of the molecule is due to a single, nearly perfectly transmitted mode, clarifying the structure of the junction. The Pt-H_2-Pt system may well form a benchmark for future molecular electronics calculations.

CO and benzene junctions. We have completed the measurements of CO junctions. The conductance histogram suggests that there are two stable configurations, one with a conductance of about $1G_0$ and one with a lower conductance, 0.6 G_0. According to our calculations the structure at low conductance may be explained by a CO molecule sitting nearly aligned with the axis of the junction. However, despite many efforts and many different configurations considered we cannot obtain good agreement with calculations for the structure near $1G_0$. In particular it is hard to find an explanation for vibration modes near 70 and 110 meV. The important message is that simple models of molecular junctions may not agree with the structures actually formed.
For Pt junctions with benzene we find stable structures with conductance in the range just above $1G_0$ and for G between $0.2G_0$ and $0.4G_0$. In the low conductance regime we identified an internal vibrational mode of the molecule rather than a metal-molecule vibration as in the case of hydrogen.

S-Au-S nanocontacts. We have prepared Au-S-Au junctions by electrochemical deposition. The molecules are deposited in a submanolayer coverage on a flat surface and then studied at low temperatures with STM tip. This method offers an interesting alternative to evaporation allowing to deposit a large variety of molecules. Experimentally we find two stable configurations with conductance of 0.2-0.3 G_0 and 0.6-0.8 G_0, which are identified using theoretical calculations, explaining the opposite dependence of the conductance upon stretching.

Partly-occupied Wannier functions. Theoretically, in order to carry out accurate calculations of coherent transport in molecules, an important issue is the quality of the basis set used to expand the electronic wave functions. We have developed a technique by which we construct partly occupied Wannier functions which are well suited for conductance calculations. The Wannier functions have the feature of exactly reproducing results of high-quality planewave based calculations. At the same time only very few Wannier functions are needed in practice and they are spatially well localized. Furthermore, they often resemble atomic orbitals or simple combinations of atomic orbitals allowing for detailed chemical analysis of the transport properties. The Wannier function technique has been used to study structure, dynamics, and electron transport of several small molecules including hydrogen, carbonmonoxide, benzene and sulfur.

5. Instrumental developments. We have developed a force sensor integrated in a mechanically controllable break junction. The instrument is based on a quartz tuning fork and allows the measurement of forces in single-atom contacts, tunnel-junctions and single-molecule junctions. It has been demonstrated for gold atomic contacts. In a parallel effort we have also developed a low temperature AFM based on a tuning fork force sensor. This instrument allows us to perform spectroscopic measurements on e-beam patterned samples (essential for gating the junctions).

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

One of the aspects of atomic chains that we explored was the *Stability against Peierls distortions*. We have found no evidence of a Peierls transition for down to temperatures of 300 mK, but that does not rule out these effects, lower temperatures will be necessary.

We were quite succesful in our experiments with single-molecule junctions in the case of very small molecules. We tried to extend our investigation to longer molecules using several different strategies. Only recently we have obtained reliable results at room temperature.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

In spite of excellent evaluation by the referees it was not possible for our consortium to apply to SONS II because 3 of the 5 teams involved were from The Netherlands and Denmark who do not participate in SONS II.

Networking with other CRPs, in particular the 3 joint meeting of SASMEC, FUNSMARTs and NANOSYN, have resulted in new collaborations between some of the members of SASMEC and some of the members of the other consortia. An ITN Marie Curie proposal has been recently submitted.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

Molecular electronics is an area whose development could have a strong impact.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

It is excellent to have the possibility of funding for meetings between several groups within the programme. We think that this is one of the most important added values of the EUROCORES programme. It has offered the possibility of building bridges between groups from different disciplines sharing scientific objectives. These interdisciplinary interactions are difficult to encourage through national funding agencies.

Our experience with the 3 annual joint-meetings of the SASMEC, FUNSMARTs and NANOSYN consortia is excellent. It offered the unique opportunity of making experimental physicist, theoretical chemists and electrochemists sit together and discuss a commom problem. In our experience the EUROCORES program has not only encouraged interdisciplinary research accross european countries, but has also indirectly reinforced interdisciplinary national networking, leading to new stable collaborations.

In the same line of facilitating interdisciplinary work, initiatives as the organization of a brainstorm meeting bringing together different EUROCORES programs, one from the

Physics, Materials and Nanosciences, SONS, and one from the life sciences, EURODYNA, like the one organized in Brussels, 27 September 2006 are, are highly appreciated and useful to weave interdisciplinary networks.

Another additional benefit is receiving timely information about other ESF activities related to the work carried out by other CRP's within the SONS program. One of the members of our CRP (Marisela Vélez) attended the ESF research Conference: Biological Surfaces and Interfaces: Biomaterials, Biosensors and analytical techniques organized by Bengt Kasemo y Marcus Textor (from the NANO-SMAP CRP).

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The overall procedures are fine. We have some complaints with the national funding agencies, in particular with the Spanish one: their representative attended just the first meeting, the Spanish groups got their funding much later than the rest.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

1. **Stretching dependence of the vibration modes of a single-molecule $Pt–H_2–Pt$ junction.** D. Djukic, K.S. Thygesen, C. Untiedt, R.H.M. Smit, K.W. Jacobsen and J.M. van Ruitenbeek, Phys. Rev. B., Rapid Commun. **71** (2005) 161402.
2. **Evidence for a single hydrogen molecule connected by an atomic chain.** M. Kiguchi, R. Stadler, I.S. Kristensen, D. Djukic, and J.M. van Ruitenbeek, Phys. Rev. Lett. **98** 146802 (2007).
3. **Electronic transport throught atomic-sized sulfur junctions between gold electrodes,** C. Arroyo, I.S. Kristensen, R. Smit, M. Vélez, G. Rubio-Bollinger, K.W. Jacobsen, N. Agrait, Submitted to Physical Review B (2007).
4. **The Mechanical Properties of an Interatomic Metallic Bond,** C. Arroyo, J.J. Riquelme, T. Frederiksen, G.Rubio-Bollinger, M. Brandbyge, N. Agraït, in preparation.

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

1. **Stretching dependence of the vibration modes of a single-molecule $Pt–H_2–Pt$ junction.** D. Djukic, K.S. Thygesen, C. Untiedt, R.H.M. Smit, K.W. Jacobsen and J.M. van Ruitenbeek, Phys. Rev. B., Rapid Commun. **71** (2005) 161402.
2. **Evidence for a single hydrogen molecule connected by an atomic chain.** M. Kiguchi, R. Stadler, I.S. Kristensen, D. Djukic, and J.M. van Ruitenbeek, Phys. Rev. Lett. **98** 146802 (2007).
3. **Electronic transport throught atomic-sized sulfur junctions between gold electrodes,** C. Arroyo, I.S. Kristensen, R. Smit, M. Vélez, G. Rubio-Bollinger, K.W. Jacobsen, N. Agrait, Submitted to Physical Review B (2007).
4. **The Mechanical Properties of an Interatomic Metallic Bond,** C. Arroyo, J.J. Riquelme, T. Frederiksen, G.Rubio-Bollinger, M. Brandbyge, N. Agraït, in preparation.
5. **Oxygen enhanced atomic chain formation.** W.H.A. Thijssen, D. Marjenburgh, R.H. Bremmer and J.M. van Ruitenbeek, Phys. Rev. Lett. **96** (2006) 026806.
6. **A force sensor for atomic point contacts.** A.M.C. Valkering, A.I. Mares, C. Untiedt, K. Babaei Gavan, T.H. Oosterkamp and J.M. van Ruitenbeek, Rev. Sci. Instrum., **76** (2005) 103903.
7. **Atomic size oscillations in conductance histograms of gold nanowires and the influence of work hardening.** I.K. Yanson, O.I. Shklyarevskii, Sz. Csonka, H. van Kempen, S. Speller, A.I. Yanson and J.M. van Ruitenbeek, Phys Rev Let., **95** (2005) 256806.
8. **Simple model systems: from atoms to molecules.**, J.M. van Ruitenbeek and D, Djukic, in: "Single molecule electronics", M. Reed, editor, Oxford University Press (2007), in print
9. **Shot noise measurements on a single molecule.** D. Djukic and J.M. van Ruitenbeek, Nano Lett. **6** (2006) 789—793.
10. **Transport at the atomic scale: atomic and molecular contacts.** A. Levy Yeyati and

J.M. van Ruitenbeek, Les Houches, Session LXXXI, 2004 on Nanophysics: Coherence and Transport, H. Bouchiat, Y. Gefen, S. Guéron, G. Montambaux and J. Dalibard, eds., (Elsevier, Amsterdam, 2005) 495-535.

11. **Distribution of conduction channels in nanoscale contacts: evolution towards the diffusive limit,** J. J. Riquelme, L. de la Vega, A. Levy Yeyati, N. Agrait, A. Martin-Rodero and G. Rubio-Bollinger, Europhysics Letters **70**, 663 (2005).
12. **Universal features of electron-phonon interactions in atomic wires,** L. de la Vega, A. Martin-Rodero, N. Agrait, A. Levy Yeyati, Phys. Rev. B **73,** 075428 (2006).
13. **Mechanical properties of metallic nanojunctions**, G. Rubio-Bollinger, J.J. Riquelme, N. Agraït, S. Vieira, in Nanotribology, E. Gnecco, E. Meyer (eds.), Springer-Verlag (2006).
14. **Modeling inelastic phonon scattering in atomic- and molecular-wire junctions,** M. Paulsson, T. Frederiksen, and M. Brandbyge, Phys. Rev. B 72, 201101(R) (2005).
15. **Inelastic Transport through Molecules: Comparing First-Principles Calculations to Experiments,** Magnus Paulsson,T. Frederiksen, and M. Brandbyge, Nano Lett. . 6, 258-262 (2006).
16. **Phonon scattering in nanoscale systems: Lowest order expansion of the current and power expressions,** M. Paulsson, T. Frederiksen, M. Brandbyge, Journal of Phys.: Conf. Series **35**, 247-254 (2006).
17. **Theory of elastic and inelastic transport from tunneling to contact,** N. Lorente, M. Brandbyge, In *Scanning Probe Microscopies Beyond Imaging*, Ed. P. Samori, (2006) Wiley-VCH, Weinheim, Chap. 15. (ISBN: 3-527-31269-2)
18. **Inelastic transport theory from first-principles: methodology and applications for nanoscale devices,** T. Frederiksen, M. Paulsson, M. Brandbyge, A.-P. Jauho, Phys. Rev. B, in press.
19. **Inelastic Finger- prints of Hydrogen Contamination in Atomic Gold Wire Systems,** T. Frederiksen, M. Paulsson, M. Brandbyge, Proc. of the ICN+T2006 conference, Basel, J. of Phys.: Conf. Series.
20. **From tunneling to contact: Inelastic signals in an atomic gold junction,** T. Frederiksen, M. Paulsson, M. Brandbyge, N. Lorente, Phys. Rev. B, in press.
21. **A low temperature Tuning Fork AFM,** R.H.M. Smit, B. Lasanta, C.R. Arroyo, M. Vélez, G. Rubio-Bollinger, N. Agraït, submitted to Rev. Sci. Instr. (2007)

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Nanotechnologie. J.M. van Ruitenbeek, NVOX, januari 2004, 37-39 (in Dutch).

Het atoom als gereedschap; de zin en onzin van nanotechnologie. J.M van Ruitenbeek, De Academische Boekengids, no. 49, maart 2005, pp.13-15 (in Dutch).

Silver nanoswitch. Jan van Ruitenbeek, Nature **433**, (2005) 21.

Life-action alloy nanowires. J.M. van Ruitenbeek, Nature Nanotechnology **1** (2006) 164-165.

Stemmen van een molecuul. Darko Djukic en Jan van Ruitenbeek, Nederlands Tijdschrift voor Natuurkunde **73-1** (2007) 10-11 (in Dutch).

Bienvenidos al nanomundo, N. Agraït, interview in El País Semanal (weekly supplement of Spain most important newspaper) (23 April 2006).

1 D. Patents and industry collaborations

Collaboration with Atomistix A/S (www.atomistix.com): Industrial Ph.D. project (MIC).

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

Coordination meetings of CRP SASMEC

Coordination meetings for SASMEC were planned and held during various workshops, most of them organized within the EUROCORES in SONS programme. First coordination meetings:

- Workshop on "Dynamics of Interacting Electrons in Quantum Wires" Miraflores de la Sierra, Spain, 29 sept- 3 oct. 2003.
- EUROCORES SONS Programme Inaugural Science Events, Strasbourg, France, May 24-25, 2004.

We held annual coordination meetings for SASMEC coinciding with the three joint meetings organized in conjunction with FUNSMARTs and NANOSYN:

- EUROCORES-SONS Workshop on Transport through Single Molecules, Leiden, The Netherlands, March 7–12, 2005 (Joint meeting SASMEC-FUNSMARTs-NANOSYN)
- EUROCORES-SONS Workshop on Functional Molecular Nanostructures –Kloster Irsee, Germany, April 26th – 29th, 2006 (Joint meeting SASMEC-FUNSMARTs-NANOSYN)
- EUROCORES-SONS Workshop on Molecular Nanoelectronics, Veilbronn, Germany, March 28th - 31th, 2007 (Joint meeting SASMEC-FUNSMARTs-NANOSYN)

An additional ccordination meeting was held in

- EUROCORES-SONS Conference 2006, San Guiliano Terme, Italy, June 28th- July 1st, 2006 (General SONS conference)

Participation of SASMEC in the coordination meeting of NANOSYN, held in Madrid, 30 Sept-1 Oct 2005. The goal is to combine efforts and search common strategies.

Visits

Kristian Thygessen visited Jan for a week (13-18 Oct 2003).
Nicolas Agrait was visiting the DTU at Lyngby, for one week (beginning of December 2004).
Thomas Frederiksen visited Madrid for one week the third week of February 2005.
Jan van Ruitenbeek visited FUNSMART partner prof. Christian Schönenberger (28 Nov. 2006).
Iben Kristensen visited Jan van Ruitenbeek's lab (feb. 27 – march 3, 2006).

1 F. Participation in other conferences

Please list only the most relevant

2003-2004

1. N. Agraït (invited talk). "Transport, Forces and Vibration Modes in a Chain of Single Gold Atoms", 3rd SFB 513 Workshop 2003 and Krupp Symposium, Nanostructures at Surfaces and Interfaces, Konstanz, Germany (6-9 July 2003).
2. N. Agraït (invited talk). "Atomic-Sized Conductors: Achievements and Challenges", Workshop on Electrical and Mechanical Properties of Nanowires Venice, Italy (17-24 August 2003).
3. G. Rubio-Bollinger (invited talk). "Conduction Channels in Nanoscale Contacts: From one Atom to the Diffusive Limit", Electrical Transport in Nanowires, Venice, Italia (5-11

September 2004).

4. J.M. van Ruitenbeek (invited talk), 1st annual meeting of the Copenhagen Graduate School for Nanoscience and Nanotechnology, Copenhagen, Denmark (3.12.03).
5. J.M. van Ruitenbeek (invited talk), Vth Rencontres de Moriond in Mesoscopic Physics, La Thuile, Italy (31.1.04).
6. J.M. van Ruitenbeek (invited talk), Int. Workshop on Advances in Molecular Electronics: from Molecular Materials to Single-Molecule Devices, Dresden, Germany (23.2.04).
7. J.M. van Ruitenbeek (invited talk), Les Houches Summerschool Session LXXXI on "Nanoscopic Quantum Physics" 2004 (four lectures) (12-22.7.04).
8. J.M. van Ruitenbeek (invited talkW.E. Heraeus Summer school "Molecules : Building Blocks for Future Nano Electronics", Wittenberg, Germany (two lectures) , (2-13.8.04).
9. J.M. van Ruitenbeek (invited talk), "Premières rencontres Grenobloises d'électronique moléculaire", ELECMOL'04 (16-17.9.04).
10. J.M. van Ruitenbeek (invited talk) Rundgespräch in preparation of a DFG programme "Quantum Transport at the Molecular Scale", Paderborn, Germany , (22-23.11.04).
11. M. Brandbyge, "Density functional calculations of elastic and inelastic electron transport in atomic scale conductors", invited talk, NAREGI workshop on electron transport, excitation and correlation in nanoscience, CRIS, Hokkaido Univ., Sapporo, Japan. (Oct. 2004).

2005

12. N. Agraït (invited talk), *Atomic Chains: Wires Formed from Metal Atoms*, 15th NID Workshop, Madrid, Spain, (31 January-2 February 2005).
13. J.M. van Ruitenbeek (oral,invited), *Quantum properties of atomic-sized conductors: Single atoms, chains of atoms, and molecules*, nanoPhys2005 Tokyo (26.01.05).
14. J.M. van Ruitenbeek (oral,invited), "Quantum properties of atomic-sized conductors: Single atoms, chains of atoms, and molecules" March meeting of the Condensed Matter Devision of the American Physical Society, Los Angeles, USA, (21-25.03.05)
15. J.M. van Ruitenbeek (oral,invited)., "Transport at the atomic scale: atomic and molecular contacts" Niels Bohr Sommer Institute, University of Copenhagen, Denmark, (21-24.08.05).
16. J.M. van Ruitenbeek (oral,invited)., "Quantum properties of atomic-sized conductors: Single atoms, chains of atoms, and molecules", Karlsruhe CFK Summer School in Bad Herrenalb, Germany, on "Nano-Electronics", (1-4.09.05).
17. J.M. van Ruitenbeek (oral,invited), "Quantum properties of atomic-sized conductors: Single atoms, chains of atoms, and molecules", Psi-K-2005 conference, Swaebische Gmund, Germany (19.09.05).
18. J.M. van Ruitenbeek (oral,invited), "Simple molecules as benchmark systems for molecular electronics", Bat Sheva Seminar on "Electron Transport in Molecular Junctions" East-Galilea, Israel, (19-22.09.05).
19. J.M. van Ruitenbeek (oral,invited), "Electrical transport through atomic and molecular wires", Leuven/Antwerpen School on "Molecular Biophysics" Retie, Belgie, (3-7.10.05).
20. J.M. van Ruitenbeek (oral,invited), "Simple molecules as benchmark systems in molecular electronics." PACIFICHEM 2005, Honolulu, Hawaïï (16-19.12.05)
21. M.Brandbyge (invited talk), "Electron-current induced inelastic effects in atomic nanostructures", European Conference on Surface Science (ECOSS-23), Berlin (September 2005).
22. M. Brandbyge (invited talk), "Elastic and inelastic transport from density functional theory", Niels Bohr, Summer Symposium on "Transport in mesoscopic and single-molecule systems" (August 2005).
23. M. Paulsson, "Inelastic transport through molecules: Comparing first-principles calculations to experiments" talk at conference, Elecmol'05, Grenoble, France (December

2005).

24. M. Paulsson, “Inelastic scattering in molecular conductors: Lowest order expansion”, Workshop on Progress in non equilibrium Green’s functions, Kiel, Germany (September 2005).

2006

25. N. Agraït (invited talk), “Electronic Transport and Mechanical Properties of suspended atomic chains of gold”, International Conference on Nanoscience - ICON2006, Choroní, Venezuela, 7-11 Mayo, 2006.
26. N. Agraït (invited talk), "Electron transport through gold atomic wires and simple molecules", CREST workshops on physics of single molecules: Transport properties of single molecules atomic wires and DNA”, Kanagawa, Japan 16-18 May 2006.
27. N. Agraït (invited talk), “Metal nanowires – I” and “Metal nanowires – II”, Summer School on Metal Clusters and Surfaces, Pisa (Italy) 3-6 July 2006.
28. N. Agraït (invited talk), "Electron transport through gold atomic wires and simple molecules", Canadian Institute for Advanced Research (CIAR) Nanoelectronics program Banff National Park, Canada, 9-12 November 2006.
29. N. Agraït (invited talk), "Inelastic effects in electron transport through gold atomic wires", CECAM workshop on Inelastic effects in transport at the atomic scale: from realistic current simulations to chemical detection at the atomic scale via IET spectroscopy, Lyon, France, 18-20 December 2006.
30. J.M. van Ruitenbeek (invited talk), MRS spring meeting San Francisco, USA (17-21.6.2006).
31. J.M. van Ruitenbeek (invited talk), CREST workshops on "Transport properties of single molecules and atomic wires", Kanagawa, Japan 16-18 May 2006.
32. J.M. van Ruitenbeek (invited talk), Workshop “Spin and charge effects at the nanoscale” (SCEN06) Pisa, Italy. (three lectures) (1-6.6.06).
33. J.M. van Ruitenbeek (invited talk), Advanced Research Workshop Nanopeter 2006, St. Petersburg, Russia (24-30.06.06).
34. J.M. van Ruitenbeek (invited talk), Rencontres de Vietnam, Hanoi, Vietnam (6-12.08.06).
35. J.M. van Ruitenbeek (invited talk), Summerschool “Fundamentals of nanoelectronics”, Lake Balaton, Hungary (28-1.08.06).
36. Mads Brandbyge (invited talk), ”DFT calculations of inelastic electron transport in atomic wire structures: heating and damping ”, CECAM workshop on inelastic effects in atomic-scale transport , Lyon, France, Dec. 2006.
37. M. Brandbyge (invited talk), "Transport in molecules and nanowires from Density Functional Theory", SMS2006 - Spanish Molecular electronics Symposium, San Sebastian, Spain, March 2006.
38. M. Brandbyge (invited talk), Electron-vibration interaction in atomic-scale conductors: Inelastic transport and heating", 3rd Nanospain workshop, Pamplona, Spain, March 2006.
39. M. Paulsson (invited talk), “Inelastic scattering from DFT : Selection rules explained”, CECAM workshop on inelastic effects in atomic scale transport, Lyon, France, Dec. 2006.

2007

40. N. Agraït (invited talk), “Mechanical properties and dynamics of suspended atomic chains”, CECAM workshop on Multiscale approaches to Nanomechanics, Lyon, France, Feb. 5-7, 2007.
41. N. Agraït (invited talk), “Electronic Transport and Mechanical Properties of suspended atomic chains of gold”, 13th Brazilian Workshop of Semiconductor Physics (BWSP13), São Paulo, Brazil, April 1-5, 2007.
42. N. Agraït (invited talk), International Workshop on Electron transport through a linked mlecule in nano-scale , in Hongo (Japan), Aug. 18-20, 2007.
43. J.M. van Ruitenbeek (invited talk), The 384 Hereaus Seminar on "Nonequilibrium

Transport of Strongly Correlated Systems: Towards Simulation of Novel Devices", Bad Honnef, Germany (31.1.07-2.2.07).

44. M. Brandbyge (invited talk), "Calculations of Molecular Electronics with the DFT/NEGF Method ", invited talk, American Physical Society March meeting, Denver CO, USA, March 2007.

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

R.H.K. Smit, postdoc (1st May 2004 - 30th April 2007) [IP 1]

A.M.C. Houkes-Valkering, postdoc (1st September 2003 – 31st August 2004) [IP 2]

A.I. Yanson, postdoc (1st September 2004 – 31st september 2006) [IP 2]

M. Paulsson, postdoc (1st February 2004 - 31st January 2007) [IP 3]

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (e.g. 02-PE-SONS-070): 02-PE-SONS-070 Acronym / Short Title: NOMSAN Full Title: **NOVEL OPTICAL METHODS FOR SELF ASSEMBLED NANOSTRUCTURES** Project Leader name: K Dholakia Project Leader affiliation: University of St Andrews institutional home page (URL): www.st-and.ac.uk project-related home page (URL): www.st-and.ac.uk/~atomtrap Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1 …
Principal Investigator (name & affiliation): Kishan Dholakia, University of St andrews
Total Funding amount of the IP *(to be corrected by the PI)*
AP 1
Principal Investigator (name & affiliation): Prof L Torner **ICFO– The Institute of Photonic Sciences** Mediterranean Technology Park Av. del Canal Olímpic s/n 08860 Castelldefels (Barcelona), Spain Tel.: (+34) 93 553 40 01 Fax: (+34) 93 553 40 00 E-mail: lluis.torner@icfo.es

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The grant has been exceptionally successful in terms of major internationally visible output in the individual RPs. Projects that would not have happened without detailed discussions, joint experimental and theoretical work include in particular studies on surface plasmon enhanced trapping. Major areas of advance are:

- **Large scale arrays: published work on creation of large scale evanescent wave trap arrays.**
- **Creation of an acousto-optic deflector trapping system for large scale studies of colloid**
- **Creation of the first ever dielectric resonator trap guiding and trapping colloid**
- **Optical sorting of red and white blood cells in a large scale periodic landscape created by using a Bessel beam**
- **Generation of an optical conveyor belt using Bessel beams for nanoparticle delivery**
- **Use of photonic crystals to create form birefringent microcogs useful for rotation**
- **Generation and study of white light Bessel beams for optical trapping and biophotonics**
- **Detailed study of equilibria positions and understanding of transport in light fields for sorting**
- **Creation of colloidal structures as quasi crystalline materials ands observation of diffraction patterns**
- **Developments of Raman spectroscopy of trapped objects particularly in a fibre trap**
- **Optical binding and bistability for two spheres**
- **Measurement of the enhanced optical forces on a single probe particle exposed to the surface plasmon at a homogeneous gold/water interface.**
- **Elucidation of the enhanced optical forces between metal nanoparticles supporting localized surface plasmon resonances.**
- **Demonstration of parallel and selective trapping at a patterned gold surface.**
- **Observation of optical solitons and modulational instability in condensed matter**

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

We achieved a major joint paper and several major conference papers from the CRP but also realised it was more advantageous and productive to perform other strands of work separately with joint meetings for mutual awareness

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term

strategies- next 2/3 years)

None at this stage, but we are in discussions over this topic. We did submit a SONSII proposal that was unsuccessful at the second round

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

Extended organization of colloidal microparticles by surface plasmon polariton excitation, V. Garcés-Chávez, R. Quidant, P. J. Reece, G. Badenes, L. Torner, K. Dholakia, Phys. Rev. B **73**, 085417 (2006)

Four invited talks are partly based on this work.

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

Parallel and selective trapping in a patterned plasmonic landscape,
M. Righini, A. S. Zelenina, C. Girard, R. Quidant, Nature Phys. 3, advanced online publication (2007) DOI:10.1038/nphys624

Enhanced optical forces between coupled resonant metal nanoparticles,
A. S. Zelenina, R. Quidant, M. Nieto-Vesperinas, Opt. Lett. 32, 1156-1158 (2007)

Surface plasmon radiation forces,
G. Volpe, R. Quidant, G. Badenes, D. Petrov, Phys. Rev. Lett. 96, 238101 (2006)

Tunable optical sorting and manipulation of nanoparticles via plasmon excitation,
A. S. Zelenina, R. Quidant, G. Badenes, M. Nieto-Vesperinas, Opt. Lett. 31, 2054- 2056 (2006)

Extended organization of colloidal microparticles by surface plasmon polariton excitation,
V. Garcés-Chávez, R. Quidant, P. J. Reece, G. Badenes, L. Torner, K. Dholakia, Phys. Rev. B 73, 085417 (2006)

Radiation forces on a Rayleigh dielectric sphere in a pattened optical near field,
R. Quidant, D. V. Petrov, G. Badenes, Opt. Lett. 30, 1009-1011 (2005)

Light-induced cell separation in a tailored optical landscape
L. Paterson, E. Papagiakoumou, G. Milne, V. Garcés-Chávez, S. A. Tatarkova, W. Sibbett, F. J. Gunn-Moore, P. E. Bryant, A.C. Riches and K. Dholakia , Appl. Phys. Lett. 87 123901 (2005) Also selected in the Virtual Journal of Biological Research

White light propagation invariant beams
P. Fischer, C. Brown, J. Morris, C. López-Mariscal, E. Wright, W. Sibbett, and K. Dholakia, Opt. Express 13, 6657-6666 (2005)

All-optical control of microfluidic components using form birefringence
S.L. Neale, M. P. MacDonald, K. Dholakia and T. F. Krauss, Nature Materials 4, 530–533 (2005)

Optical conveyor belt for delivery of submicron objects
T. Cizmár, V. Garcés-Chávez, K. Dholakia, and P. Zemánek, Appl. Phys. Lett. 86, 174101 (2005)

Extended-area optically induced organization of microparticles on a surface
V. Garcés-Chávez, K. Dholakia, and G. C. Spalding, Appl. Phys. Lett. 86, 031106 (2005)

Observation of bistability and hysteresis in optical binding of two dielectric spheres
N.K. Metzger, K. Dholakia, and E.M. Wright Phys. Rev. Lett. 96 068102 (2006)

Experimental Observation of Modulation Instability and Optical Spatial Soliton Arrays in Soft Condensed Matter
P. J. Reece, E. M. Wright, K. Dholakia, Phys Rev Lett 98, 203902 (2007)

Fractionation of polydisperse colloid with acousto-optically generated potential energy landscapes
Graham Milne, Daniel Rhodes, Michael MacDonald and Kishan Dholakia, Optics Letters 32, 1144 (2007)

Measurement of the restoring forces acting on two optically bound particles from normal mode correlations
N.K. Metzger, R.F. Marchington, M. Mazilu, R.L. Smith, K. Dholakia, E.M. Wright, Phys. Rev. Lett. 98, 068102 (2007)

Optical vortices produced by diffraction from dislocations in two-dimensional colloidal crystals
M MacDonald, P Prentice and K Dholakia, New J. Phys. 8 257 doi:10.1088/1367-2630/8/10/257

Wavelength dependent propagation and reconstruction of white light Bessel beams
P Fischer, H Little, R L Smith, C Lopez-Mariscal, C T A Brown, W Sibbett and K Dholakia, J. Opt. A: Pure Appl. Opt. 8 477-482

A dual beam fibre trap for Raman microspectroscopy of single cells
P. R. T. Jess, V. Garcés-Chávez, D. Smith, M. Mazilu, L. Paterson, A. Riches, C. S. Herrington, W. Sibbett, and K. Dholakia, Opt. Express 14, 5779-5791 (2006)

Interference from multiple trapped colloids in an optical vortex beam,
W. M. Lee, V. Garcés-Chávez, and K. Dholakia, Opt. Express 14, 7436-7446 (2006)

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Tweezer pleaser, highlight in Nature **447**, 357 (2007)

Puntos de oro, El País (article in the Spanish most read news paper), 23rd May (2007)

The Scotsman newspaper (2006)

Invited Book chapter: K Dholakia et al. Methods in Cell Biology (2007): colloidal and cellular separation using optical forces

Invited Book chapter: K Dholakia Methods in Cell Biology (2007): Near field optical micromanipulation

1 D. Patents and industry collaborations

Method of optical manipulation of small-sized objects, M. Righini and R. Quidant, European patent filled. Application reference: 06125242.5-2208

Fractionation of polydisperse particles

K Dholakia, M MacDonald, G Milne European patent filed Sept 2006

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF

We have had ~ 3meetings/per year in the last three years. Details will be supplied later

1 F. Participation in other conferences

Please list only the most relevant

(not a complete list)

- **Micro- and nano- manipulation with plasmon light**, Romain Quidant, Invited talk, International workshop on plasmonics and applications in nanotechnologies, Singapore, December 2006
- **Micro- and nano- manipulation with plasmon light**, Romain Quidant, Invited talk**,** Nanometa 2007, Seefeld, Austria, January 2007
- **Plasmon based-optical manipulation**, Romain Quidant, Invited talk**,** CLEO Europe 2007, Munich, Germany, June 2007
- **Plasmon-based optical manipulation: a route towards ultra gentle nanotweezers**, Romain Quidant, Invited talk**,** Frontiers in Optics 2007, San Jose, USA, September 2007
- **Light takes hold: Optical binding and biophotonics**; K Dholakia, invited talk, LATSIS, Laussanne, June 2007
- **Optical micromanipualtion takes hold; plenary talk,** K Dholakia, CLEO-Europe. June 18th 2007
- **Optical micromanipulation for Biophotonics, Invited Talk,** Taiwan, Sept 2006, Optics Within the Life Sciences, Taiwan, 2006

- **New frontiers in biophotonics,**
  ABPB conference, Invited Talk, Cairns, Australia, July 2007

- **New directions in Optical Vortices,**
  Kishan Dholakia, Sapporo, Japan, Invited Talk July 2007

- **Optical Binding**
  Kishan Dholakia, Invited Talk, PIERS conference, Boston, USA, March 2006

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

St Andrews personnel (ICFO to be added)

We had several strands of work at St Andrews and we made optimal use of monies by employing personnel with appropriate experience for the various parts and using part funding as appropriate. This was a major asset ensuring we obtained the best results for our individual RP as shown in the publication lists.

For the joint CRP, V Garces-Chavez and P Reece were the key PDRAs working with ICFO

Daniel Rhodes (PhD achieved Sept 2005)	1/8/04-31/12/04 (50%) and 1/10/05-31/12/06. (Sorting fractionation)
Peter Reece, PDRA, (solitons, surface traps)	1/2/07-30/6/07
Graham Milne, (PHD achieved 2007)	1/11/06-31/1/07
V Garces-Chavez (plasmons. Surface traps))	1/1/04-31/7/04 and 31/12/06/31/5/07
F Akerboom (technician)	1/1/04-30/6/04 (20%) 1/7/05-30/6/06 1/7/06-30/6/07
WM Lee (vortices, coherence)	1/2/06-31/1/07 (80%) 1/2/07-30/6/07 (100%)
M Mazilu (Raman/binding)	1/7/06-31/12/06 (50%)
A Carruthers (white light)	1/3/06-31/8/06 (20%)

EUROPEAN SCIENCE FOUNDATION

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"SPENSA – Surfactant PolyElectrolyte Nanostructure Self-Assembly"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number ():02-PE-SONS-064-SPENSA Acronym / Short Title: SPENSA Full Title: Surfactant PolyElectrolyte Nanostructure Self-Assembly Project Leader name: *Dr Karen Edler* Project Leader affiliation: *Department of Chemistry, University of Bath* Institutional home page (URL): *www.bath.ac.uk* Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator (name & affiliation): Dr Karen J. Edler, Department of Chemistry, University of Bath, UK
Total Funding amount of the IP *(to be corrected by the PI)£207 622*
IP 2
Principal Investigator (name & affiliation): Dr Jean-Louis Sikorav, Laboratoire de Biophysique de l'ADN, DBJC/SBGM, CEA Saclay, France
Total Funding amount of the IP *(to be corrected by the PI) 0*€

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The work carried out in this CRP has necessarily been limited to the project at Bath, since no funding was ever obtained for those parts of the project which were to have occurred in Saclay. Although we have had CRP meetings for joint discussion of our results, lack of support meant that only resources & expertise available in Bath were directly used during the project, which crippled from the outset the possibility of achieving what we set out to do.

However work at Bath has conformed to that initially proposed and we have made substantial steps towards understanding formation of self-organised surfactant-templated films, and developed our novel polymer-surfactant films towards applications. During the project we have carried out 10 neutron scattering experiments at ISIS and 3 ESRF experiments (one in collaboration with ID10B beamline scientist Dr L. Cavalcanti) to study our films. We have published 4 papers on polymer film work, and 2 on silica-surfactant investigations related to this project. A further paper is currently submitted with 3 more in preparation. The work was reported in 19 invited and 10 other talks by SPENSA members over the last three years, including 3 keynote lectures. In summary:

- we have investigated & proposed formation mechanisms for surfactant templated thin films that grow at the air-solution interface, both silica and polymer based.
- we have found new film forming systems which are more generally applicable to a wide range of polymers including biocompatible polymers, expanding the scope for applications of these novel membranes
- we have formed robust cross-linked polyelectrolyte-surfactant films which maintain their mesoscale structure after drying, also an essential step towards applications
- we have investigated applications of the polymer films in encapsulation & further templating to form novel inorganic-polymer/surfactant membranes.
- we have prepared silica & phenyl-silica materials suitable for DNA encapsulation experiments

At the beginning of the project, our first priority was to investigate polyethylenimine-cetyltrimethylammonium bromide (PEI-CTAB) films which form spontaneously at the air-solution interface, containing a well ordered nanostructure.[1] We studied variables such as surfactant headgroup type and tail length, polymer structure and molecular weight, pH, humidity and salt concentration on formation and structures within these films.[2,3] In collaboration with a research group led by Dr A Gramatges-Perez (INSTEc, Havana), we have also studied film formation and solution properties at extremely low polymer and surfactant concentrations[4] in addition to our investigations of the materials properties of this system at higher concentrations. This has enabled us to propose a formation mechanism for these films and to compare this unusual interfacial absorption behaviour with that of other polymer-surfactant systems.[5] These initial films were fragile, and difficult to remove from the solution surface so we cross-linked the polymer and found it is possible to successfully strengthen the film to prepare robust, self-supporting membranes with micron to sub-micron thickness. Further experiments confirmed that the ordered nanostructure in these membranes survives cross-linking unaltered, or in some cases enhanced, and that the nanostructure also survives removal of the membrane from the solution surface and drying.[3,5] This is essential for further use of these membranes in most applications.

During this work we also looked for ways to extend film formation from our original PEI-CTAB system to other polymer-surfactant solutions in order that this new method of membrane self-assembly could be more generally applicable. We found that membranes will form for a wide range of water soluble polymers in the presence of mixed systems containing cationic and anionic surfactants, as long as the cationic species is present in excess.[6] Polymers which have been investigated in detail for this new film forming system include DNA, polyethyelene oxide and polyacrylamide as well as PEI. Out of the wide range of possible polymers we have concentrated on those which are biocompatible in the hopes of finding applications for our materials in health-related areas such as encapsulation/release or cell scaffolds. We have also, towards this end, investigated replacing the cationic and anionic surfactant components with

more biocompatible zwitterionic surfactants, non-ionic surfactants, and long chain amines. The anionic surfactant component can be altered from sulphate-based surfactants to carboxylic acids or zwitterionic species over a wide concentration range, however the cationic component is more difficult to replace.[7] Using long chain amines did allow film formation to occur and we are still investigating the extent to which the cationic component can be substituted while maintaining film structure.

We have also begun investigations towards applications of these films in two ways. Firstly we have begun work during this project on encapsulation of hydrophobic species within the ordered micelle network in the polymer films. Results from experiments using both simple hydrophobic molecules and more complex drug molecules are promising,[7,8] and this topic is now the subject of a newly funded EPSRC grant, starting July 2007, with a PhD student and PDRA working in this area. Encapsulation, release, triggered release and effects of polymer structure will be investigated in this new study. Secondly we have used the dried films recovered from the solution surface as templates for the formation of porous inorganic materials. Initial work has been carried out on silica, and the preliminary results from the work in this project have also led to the funding of a PhD student who will begin work to extend this area, in Oct 2008. This project will optimise our silica templating procedures and investigate other inorganic materials using these novel dry nanoscale templates. Further Royal Society funding has also been obtained to continue our collaboration with the Havana group studying polymer-surfactant interactions in dilute film forming systems. Another related funding application has been submitted to the EPSRC & others are currently in preparation.

During this project the Bath group were also to continue our investigations on surfactant-templating of inorganic films, and to supply materials to the Saclay group for DNA confinement experiments. Two PhD students C. Fernandez-Martin & A.M.Hawley (not funded through SPENSA) have worked on surfactant-templating of silica and titania films, and this work has progressed alongside our insights into the related polymer-surfactant films.[9-12] A collaboration with Prof L Peter at Bath tests the titania films in dye-sensitised solar cells. Prior work at Saclay by J-L Sikorav & A. Goldar, suggested strong specific interactions between DNA and phenol-water interfaces. As part of the CRP interaction we therefore decided to prepare both plain nanoporous silicas and similar materials with phenol functionalisation to observe the differences in DNA adsorption. We therefore undertook a study of the formation mechanism and structure of phenol-functionalised surfactant templated silica films, formed through a similar mechanism to our surfactant-polymer membranes.[13] However, so far only the plain silica materials have been sent to Saclay for analysis since, owing to problems there, this analysis has not yet been done.

Work from this CRP presented at the SONS meeting in Pisa and also in Prague in 2006 led to discussions with Dr Faul from SISAM which have developed into the forthcoming workshop on Polymers, Amphiphiles and Nanostructured Materials" to be held in Bristol 13-15th June 2007. We hope that this association will continue to develop over the coming months towards an active collaboration. The SPENSA project also has led to our new and valuable collaboration with Dr Perez-Gramatges' research group in Cuba, for which we have obtained continuation funding. Funding has also been obtained for a new collaborative project with Dr Price at Bath for further development of the polymer-surfactant films.

References:

1 Edler, K. J.; Goldar, A.; Brennan, T.; Roser, S. J. *Chem. Comm.* **2003**, 1724-1725.
2 O'Driscoll, B. M. D.; Fernandez-Martin, C.; Wilson, R. D.; Roser, S. J.; Edler, K. J. *J. Phys. Chem. B* **2006**, *110*, 5330-5336.
3 O'Driscoll, B. M. D.; Milsom, E.; Fernandez-Martin, C.; White, L.; Roser, S. J.; Edler, K. J. *Macromol.* **2005**, *38*, 8785-8794.
4 Comas-Rojas, H.; Aluicio-Sarduy, E.; Rodríguez-Calvo, S.; Pérez-Gramatges, A.; Roser, S. J.; Edler, K. J. *Soft Matter* **2007**, online DOI: 10.1039/b700942a.
5 O'Driscoll, B. M. D.; Fernandez-Martin, C.; Wilson, R. D.; Roser, S. J.; Edler, K. J. *Langmuir* **2007**, *23*, 4589-4598.
6 O'Driscoll, B. M. D.; Nickels, E. A.; Edler, K. J. *Chem. Commun.* **2007**, 1068 - 1070.
7 O'Driscoll, B. M. D.; Hawley, A. M.; Cavalcanti, L.; Roser, S. J.; Edler, K. J. **2007**, in preparation.
8 O'Driscoll, B. M. D.; Hawley, A. M.; Roser, S. J.; Edler, K. J. *Langmuir* **2007**, submitted.
9 Edler, K. J.; Brennan, T.; Roser, S. J. *Thin Solid Films* **2006**, *495*, 2-10.
10 Fernandez-Martin, C.; Edler, K. J.; Roser, S. J. *Chem. Mater.* **2007**, submitted.
11 Fernandez-Martin, C.; Edler, K. J.; O'Driscoll, B. M. D.; Roser, S. J. **2007**, in preparation.
12 Hawley, A. M.; Edler, K. J.; O'Driscoll, B. M. D.; Roser, S. J. **2007**, in preparation.
13 O'Driscoll, B. M. D.; Hawley, A. M.; Roser, S. J.; Edler, K. J. *Journal of Rare-Metal Materials & Engineering* **2007**, accepted.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

The aims outlined in the original proposal were as follows:

1. to discover the formation mechanisms in thin films of self-assembled surfactant templated inorganic and polyelectrolyte materials using a range of techniques and to apply this to create new nanostructured materials
2. to propose a theoretical model of these systems using an extension to the existing theory of polyelectrolytes
3. to use the channels in the created nanostructures as reduced volume to confine DNA and perform the renaturation reaction.

These were split between the two projects as follows (from original proposal):

Bath group: experimental characterisation of both the silica-surfactant and polyelectrolyte-surfactant systems using analysis techniques that cover a range of length scales.

Saclay group: theoretical description of the hierarchical self-assembly processes will be worked out, and modeling of the formation mechanisms carried out in Dr Loïc Auvray's and Dr Alan Braslau's research groups. Once the two systems have been investigated and some understanding of the emergent structures and formation mechanisms has been gained we will attempt the renaturation of DNA at Saclay in the research group of Dr Jean-Louis Sikorav.

However no funding was ever forthcoming for the Saclay branch of the project. Thus the aims 2, & 3 above (related to Milestones 1&3) were not completed. We have, as a result of our investigations of the systems outlined in (1) proposed formation mechanisms for the thin films prepared both silica and polymer, but have not been able to link this with theoretical modelling (Milestones 1&3). Similarly we have prepared materials in the hopes of carrying out the experiments in (2) (deliverable D3, milestone M2), and have also been awarded beamtime through a competitive peer reviewed proposal round, at the LLB neutron reactor (Saclay, experiment no. 8335 on PACE) to carry out part of these experiments. However the LLB reactor has been closed down due to safety issues for many months since this experimental time was awarded last summer and we have not yet been able to schedule this experiment. A no-cost extension of 3 months was obtained from the EPSRC in order to try to have this work scheduled, and to finish other aspects of the project work; however since the PDRA working on the project will finish on 22nd May 2007 it now seems very unlikely that this experiment will be possible. Mesoporous silica monoliths for the DNA encapsulation experiments have been prepared and were sent to Saclay for initial neutron scattering analyses by Dr Auvray's group but due to the reactor problems this was also not achieved.

The Bath part of the project has achieved Milestone 2 and 4, for which we were responsible, as set out in the original proposal. We prepared films for the proposed DNA experiments, and have also prepared surfactant-templated films from a wide range of polymers, silica and titania and have applied the polymer-surfactant films as templates for inorganic materials (Deliverables D1&D2, milestones M2&M4) as well as encapsulating hydrophobic species within these novel membranes.

The Saclay branch of the project has suffered from the management of the head of the Biology Department. The head of biology department has forced Dr. Jean Louis Sikorav to change his affiliation (his is now working in the Material Science Division) and Dr. Arach Goldar to abandon the project for reasons which are still obscure. All these problems have forestalled the theoretical part of the project.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

Dr Edler is currently involved in organising a SONS workshop at Bristol with Dr Charl Faul which will involve scientists from SPENSA, SISAM, NETSOMA, SONS-AMPHI, AMPHI and NEDSPE. This interaction between Dr Faul and Dr Edler is at a preliminary stage but may in the future generate joint collaborative proposals.

She has also begun preliminary experiments on collecting small angle scattering data from tubulin with Dr Niels Galjart who is part of the ESF Euro-DYNA Programme. This collaboration was initiated through the SONS-Euro-DYNA workshop held in Brussels in late 2006 which provided a valuable opportunity to communicate between physical chemists and biologists, resulting in the trial experiments we are currently carrying out. We hope that the results of these experiments will provide interesting information and lead to further interaction.

Projects related to SPENSA funded during SPENSA project:
Royal Society International Joint Project - 2004/R1 South America and Cuba-UK, K.J. Edler, A. Pérez Gramatges (Cuba), 2 years, (2004-2006), £11 995
"Polyelectrolyte-Surfactant Interactions in Film Forming Solutions"

New, funded projects resulting from work done in the SPENSA project:
EPSRC grant EP/E029914/1, K.J. Edler & G.J. Price (Bath), 3.5 years (2007-2010) £349 475
"*Nanostructured Hydrogel Films for Encapsulation & Release*"

Royal Society International Joint Project - 2006/R1 South America and Cuba-UK, K.J. Edler, A. Pérez Gramatges (Cuba), 2 years, (2007-2009), £12 000
"Solution and Surface Characterisation of Nanocomposite Film Forming Systems"

Submitted proposals currently under consideration:
EPSRC Next Generation Facility Users call, K.J Edler (£146 595)
"*Responsive Membranes from Polymer-Surfactant Films*"

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

The EUROCORES programme gives a valuable opportunity to work on a joint project with European partners. This is an extremely useful funding instrument with relatively little administrative overhead and should be used to encourage further development of this area of self-organised nanostructures which has been started in SONS1 and SONS2. It is noticeable that much of the currently funded work is in polymeric materials and it could be valuable to re-balance the portfolio of work with more on hierarchical inorganic materials, and area where there is also currently much interesting research activity. Possibly two programmes are needed (one for polymeric materials, one for inorganic materials) but personally I believe that the two fields would benefit from more cross-fertilization of the sort which is specifically encouraged in the EUROCORES programmes via the workshops and interaction over several CRPs as well as within the CRPs. The ability to carry out fundamental research in these programmes as well as nearer application work is also a valuable feature of the programme.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

Attendance at workshops involving multiple SONS groups provided us with invaluable scientific input to our work. Comments on our work presented at Pisa and Prague led to significant new areas of enquiry which are still in progress (eg establishing the full PEI-CTAB phase diagram where other interesting phases may be found). Contacts formed through these workshops have also led to transfer of information on relevant meetings, conferences and workshops through email lists. Such contacts would not have been formed between such a disparate set of workers from a wide range of disciplines without the initial connection through the EUROCORES programme.

The light touch ESF reporting procedures have been much appreciated, and the feedback from referees on the annual reports is also a useful external gauge of the quality of work achieved (although these were timely in the first year, the delays in the second year reduced the usefulness of this mechanism somewhat – still potentially it is a very useful feature of the EUROCORES programme).

The contact through the SONS programme with the researchers in the Euro-DYNA programme has also been of great interest and is in the process of spawning a new collaborative research interaction between Dr Edler and Dr Galjart.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

This project has encountered major difficulties on the French side, due to a lack of funding from the CEA. The EUROCORES scheme did not result in a strict financial commitment of the participating organisation and this question should be addressed.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

none

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

Peer Reviewed Publications:

1. A. Goldar and J.-L. Sikorav, Eur. Phys. J. E 14, 211-239 (2004)
   DNA renaturation at the water-phenol interface
2. Benjamin M.D. O'Driscoll, Elizabeth Milsom, Cristina Fernandez-Martin, Lyndsey White, Steven J. Roser and Karen J. Edler, *Macromolecules* (2005) *38*(21); 8785-8794. DOI: 10.1021/ma050469k.
   Thin Films of Polyethylenimine and Alkyltrimethylammonium Bromides at the Air/Water Interface
3. Karen J Edler, Tessa Brennan, Stephen J Roser, *Thin Solid Films*, **495**(1-2), 2-10 (2006)
   Formation of Mesostructured Thin Films at the Air/Water Interface
4. Benjamin M. D. O'Driscoll, Cristina Fernandez-Martin, Roland D. Wilson, Stephen J. Roser and Karen J. Edler, *J. Phys Chem B*, **110**(11); 5330-5336, (2006) DOI: 10.1021/jp056032w
   Effect of Micelle Composition on the Formation of Mesostructured Polymer/Surfactant Films.
5. Benjamin M.D. O'Driscoll, E. Anne Nickels, Karen J. Edler, *Chem. Commun.*, 1068 - 1070 (2007) DOI: 10.1039/b614224a
   Formation of Robust, Free-standing Nanostructured Membranes from Catanionic Surfactant Mixtures and Hydrophilic Polymers
6. Benjamin M. D. O'Driscoll, Cristina Fernandez-Martin, Roland D. Wilson, Jessica Knott, Stephen J. Roser and Karen J. Edler, *Langmuir* (2007) **23**(8) 4589-4598 DOI: 10.1021/la063004b
   Macroscopic, Mesostructured Cationic Surfactant/Neutral Polymer Films: Structure and Cross-linking
7. Benjamin M.D. O'Driscoll, Adrian M. Hawley, Stephen J. Roser, and Karen J. Edler, *Journal of Rare-Metal Materials & Engineering*, (2007) accepted. (Proceedings of the 4th Chinese Sol-Gel Symposium & International Forum)
   Phenyl-Functionalised Mesoporous Silica Films
8. Benjamin M.D. O'Driscoll, Adrian M. Hawley, Steven J. Roser, Karen J. Edler, *Langmuir*, (2007) submitted.
   Encapsulation of Additives into Surfactant-Polyelectrolyte Films
9. Benjamin M.D. O'Driscoll, Adrian M. Hawley, Leide Cavalcanti, Steven J. Roser, Karen J. Edler (2007) in preparation
   Surface and Solution Structure of Catanionic Surfactant-Polymer Mixtures
10. Cristina Fernandez-Martin, Benjamin M. D. O'Driscoll, Karen J. Edler and Stephen J. Roser (2007) in preparation.
    Mesophase Silica Film Formation from Mixed Cationic-Nonionic Micelle Solutions
11. Adrian M. Hawley, Benjamin M. D. O'Driscoll, Karen J. Edler and Stephen J. Roser (2007) in preparation.
    Titania Films from Non-Aqueous Solutions using Fluorosurfactant Templates

Other Publications (listed since Jan 2006 only):

- K.J. Edler, B. O'Driscoll ISIS Experiment Report RB610337 "Polymer-surfactant interactions in film forming solutions using catanionic aggregates", Instrument LOQ, 6-7 May 2006
- K.J. Edler, B. O'Driscoll ISIS Experiment Report RB620094 "Drug encapsulation in film forming polymer-surfactant solutions", Instrument LOQ, 27-28 Jul 2006

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Making thin films by surfactant-templated self-assembly, 2005.
Karen Edler, RSC Materials Chemistry Forum News, Issue 10, Autumn p7-8.

1 D. Patents and industry collaborations

Dr Edler is currently exploring possible collaborations with Kraft, but these are in negotiation.

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

A meeting within SPENSA was held on 11th Dec 2006, Saclay. A meeting earlier in the year had been planned to occur during the SONS Workshop in Pisa however due to events at Saclay it became impossible for the Saclay team representatives to attend this workshop so the meeting was not held.

1 F. Participation in other conferences

Please list only the most relevant

Invited lectures (since Jan 2006)

- K Edler: *Ordered Mesoporous Thin Films - Formation and Applications*, (keynote) 4th Chinese Sol-Gel Symposium & International Forum, Wenzhou University, P.R. China, Nov 22-25th 2006.
- K Edler: *Self-Assembly of Nanostructured Polyelectrolyte-Surfactant Thin Films at the Air-solution Interface***,** 27th Latin American Congress on Chemistry and the 6th International Congress on Chemistry and Chemical Engineering, October 16th - 20th, 2006.
- K Edler: *Self-assembled polyelectrolyte-surfactant films for encapsulation & templating*. EUROCORES SONS Meeting Pisa, 28th June-1st July 2006.
- B. O'Driscoll: *Nanostructured Films Through Polymer-Surfactant Self-Assembly* EUROCORES SONS Meeting Pisa, 28th June-1st July 2006.
- K.Edler: *Self-Assembly of Mesostructured Materials Using Surfactant Templating* (upcoming) 4th European Conference on Neutron Scattering, Lund, Sweden, 25-29 June, 2007.

Other lectures (since Jan 2006)

- K Edler: *Encapsulation in Polyelectrolyte-Surfactant Nanostructured Films*, Structure and properties of self-organized amphiphilic copolymers EUROCORES SONS Workshop, Prague 4-7th Oct 2006**.**
- B**.** O'Driscoll: *Spontaneous Polymer-Surfactant Film Formation at the Air/Solution Interface* Structure and properties of self-organized amphiphilic copolymers EUROCORES SONS Workshop, Prague 4-7th Oct 2006**.**
- B**.** O'Driscoll: *Spontaneous Polymer-Surfactant Film Formation at the Air/Solution Interface* 12th International Conference on Surface & Colloid Science, Beijing Oct 15-20th 2006.
- K. Edler: *A Tale of Two Mechanisms: Comparing Mesostructure Formation in Cationic & Nonionic Surfactant-Templated Silicas* (upcoming) 15th International Zeolite Conference, Beijing, China August 12-17, 2007
- K. Edler: *Membrane formation and encapsulation in polymer-surfactant films*, (upcoming) SONS Polymers, Amphiphiles and Nanostructured Materials Workshop, Bristol, 12-15th June 2007.

Posters (since Jan 2006)

- K Edler: *Structure Formation in Polyelectrolyte-Surfactant Films*, SAS2006 XIII International Conference on Small-angle Scattering, Kyoto, Japan 9-13th July 2006.

Other invited lectures (since Jan 2006):

- K. Edler: *Polyelectrolyte-surfactant films for encapsulation*, Chemistry Research Colloquium, School of Biomedical and Molecular Sciences, University of Surrey, 1st March 2007.
- K. Edler: *Mesostructured Film Growth at the Air/Solution Interface - SANS and Reflectivity Studies*, Delft University of Technology, Faculty of Applied Sciences, Dept. Radiation, Radionuclides and Reactors, Delft, the Netherlands, 1st June 2006.

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

Dr Ben O'Driscoll, Postdoctoral Research Associate, Department of Chemistry, University of Bath, UK 22/2/04-22/5/07

Saclay Postdoc: not yet appointed

EUROPEAN SCIENCE FOUNDATION

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"FunSMARTs I"

Collaborative Research Project (CRP) (to be completed with information form the ESF database)
1. General information
Project Reference Number **02-PE-SONS-070-FUN-SMARTs** Acronym / Short Title: **FunSMARTs** *Full Title*: ***Assembly and Manipulation of Functional Supramolecular Nano-Architectures at surfaces*** Project Leader name: **M. Ruben** Project Leader affiliation: **Institute of Nanotechnology, Karlsruhe** Institutional home page (URL):**www.fzk.de/INT** Project-related home page (URL): **www.fzk.de/funsmarts** Reporting period: **to 31 / December / 2006**
2. Individual Projects (IPs), Associated Partners (APs) and Co-operating Partners (CPs) of the Collaborative Research Project (CRP)
IP 1 EPF Lausanne
Prof. Dr. Johannes V. Barth; Institut de Physique des Nanostructures (IPN)
IP 2 ICMAB (CSIC) Barcelona
Prof. Jaume Veciana; Institut de Ciencia de Materials de Barcelona
IP 3 Aarhus University
Prof. Dr. Flemming Besenbacher; Institut of Physics and Astronomy
IP 4 MPI Stuttgart
Prof. Dr. Klaus Kern and Dr. M. A. Schneider; Max-Planck-Institute for Solid State Research
IP 5 University of Twente
Prof. Dr. David N. Reinhoud; MESA^{+} Research Institute

IP 6 Consiglio Nazionale delle Ricerche Bologna
Dr. Fabio Biscarini; CNR-ISMN - Bologna Division
IP 7 University of Trieste
Dr. Alessandro De Vita; Dipartimento di Ingegneria dei Materiali
IP 8 INT Karlsruhe
Dr. Mario Ruben, Institute of Nanotechnology, Research Centre Karlsruhe

To be completed by the Project Leader of the Collaborative Research Project

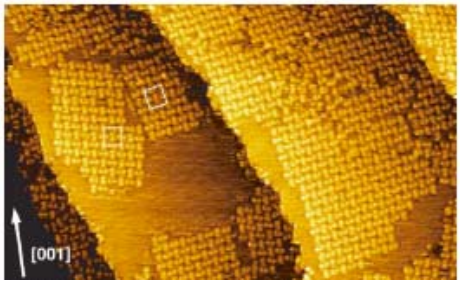
3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

Brief highlight of some scientific results of the year 2006:

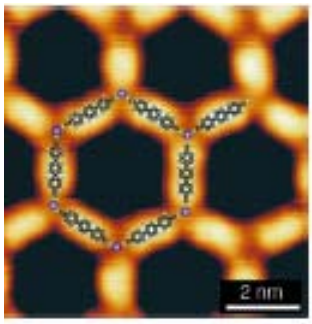
(i) **Engineering of the peptide-bonding to generate 1D H-bonded nano-strings**



Molecular squares on Ag(111)

N. Lin, S. Stepanow, F. Vidal, **K. Kern**, S. Alam, S. Strömsdörfer, S. Dremov, P. Müller, A. Landa and **M. Ruben**, Surface-Assisted Self-Assembly and Coordination Chemistry, **Dalton Trans.** 2794-2800 (2006).

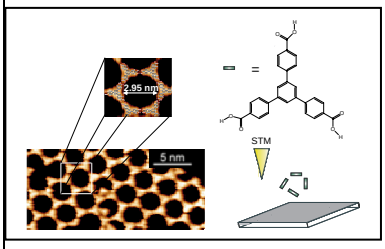
(ii) Surface-assisted Fe-coordination of Dicarboxy-diazobenzene



Co- and Fe-coordination nano-hexagons

S. Stepanow, N. Lin, D. Payer, U. Schlickum, F. Klappenberger, G. Zoppelaro, **M. Ruben,** H. Brune, **J. Barth, K. Kern** Surface-asssited Self-Assembly of 2D Metal-Organic Networks that Exhibit Unusual three-fold Coordination Symmetry, **Angew. Chem. Int. Ed.** 46, 710 - 713 (2007).

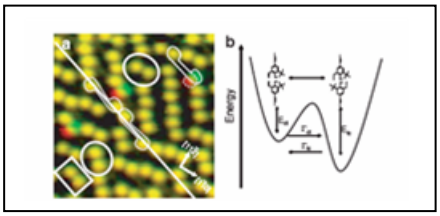
(v) Phase changes of extended trimesic acid on silver surfaces



The phase I (shown in the figure) is transformed into more densely packed phases by stepwise deprotonation of the carboxylic acid groups.

M. Ruben, A. de Vita, K. Kern et al. 2D Supramolecular Assemblies of Benzene 1,3,5-tri-yl Tribenzoic Acid: Temperature-induced Phase Transformations and Hierarchical Organization with Macrocyclic Molecules, **JACS** 15644-15651 (2006).

(vii) Powering the nanoworld



Conformational switching for an adsorbed organic molecule:. *The overlay of two STM images in (a) shows initial-final positions of the molecular tert-butyl grups in green/red, respectively.*

S. Weigelt, C. Busse, L. Petersen, K.V. Gothelf, **F. Besenbacher**, and T.R. Linderoth, Chiral switching by spontaneous conformational change in adsorbed organic molecules; **Nature Materials,** 112-117 (2006)

Also in 2006, the FunSMARTs consortium has developed along the traced scientific line as shown in the work packages A-D. In sum, 21 two-, three and even four point joint publication show the high degree of collaboration. In addition, 18 individual publications and one patent have sprung up from the activities of FunSMARTs I. Two of the results of the year 2006 were also disseminate din non-scientific journals.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

Within the frame of scientific predictability, no divergences have been observed so far. New results were generated to all work packages, of course with an increasing intensity A to D (due to the causality of the work package organisation).

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

In general, the consortium has been pursued the further intensification of the collaboration efforts in 2006. Furthermore, most of the members of the FunSMARTs consortium have joined the sequel proposal **FunSMARTs II**, which was positively evaluated for the second funding period 2006-2009. Thus, we are sure that the scientific adventure will go on.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

So far, the EUROCORES-SONS project is very successful in supporting a new trend in basic research. After finishing the second funding period in 2009/2010, a scientific similar weighted program but with an accent on application springing up from this type of research might be useful. By this way, the full potential of supramolecular organised nanostructures could be exploited by funding the integration basic and applied research. Of course, doing this will imply industrial partners, e.g. small and medium sized companies.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

To my opinion, the EUROCORES scheme is one of the most efficient network programs I have experienced. The ration between administrative and scientific effort is closed to be optimal. The considerable synergy gained by setting up such type of networking scheme is clearly based ion the possibility to bundle efficiently complementary high-level competences on the European level. In this respect it is somehow parallel to the European framework programs, but its administrative slimness speaks clearly in favour of EUROCORES. Furthermore, is the scientific competence and kind supervision of the employed ESF personal an additional point in favour of such type of EUROCORES. In short, I have a lot pleasure to work under such scheme.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

In general, the selection procedure is by far too long (especially during the first funding period). Some of the schemed ides already aged during waiting for decision.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

1. U. Schlickum, R. Decker, G. Zoppellaro, F. Klappenberger, W. Auwärter, K. Kern, H. Brune, M. Ruben, J.V. Barth : Supramolecular engineering of nanoporous chiral kagomé lattice, to be subm..
2. F. Klappenberger, M.E. Cañas-Ventura, S. Clair, S. Pons, U. Schlickum, H. Brune, K. Kern, Z.-R. Qu, Th. Strunskus, Ch. Wöll, A. Comisso, A. De Vita, M. Ruben, J.V. Barth : Conformational adaptation in supramolecular organisation of oxalic amide derivatives on Au(111), subm..
3. P. Gambardella, S. Clair, S. Stepanow, S. Pons, A. Dmitriev, J. Honolka, N. Lin, H. Brune, J.V. Barth and K. Kern : Tunable magnetic properties of Fe centers in metal-organic supramolecular surface structures, subm..
4. Willi Auwärter, Alexander Weber-Bargioni, Susan Brink, Andreas Riemann, Agustin Schiffrin, Mario Ruben, and Johannes V. Barth : Controlled metalation of self-assembled porphyrin nanoarrrays in two dimensions, **ChemPhysChem 8**, 250 (2007).
5. S. Stepanow, N. Lin, D. Payer, U. Schlickum, F. Klappenberger, G. Zoppellaro, M. Ruben, H. Brune, J.V. Barth and K. Kern : Surface-assisted assembly of 2D metal-organic networks with threefold coordination symmetry, **Angew. Chem. Int. Ed. 46**, 710 (2007).
6. D. Payer, A. Comisso, A. Dmitriev, T. Strunskus, N. Lin, Ch. Wöll, A. De Vita, J.V. Barth and K. Kern : Ionic hydrogen bonding controlling 2-dimensional supramolecular systems at a metal surface, **Chem. Eur. J 13**, 3900 (2007).
7. S. Stepanow, N. Lin, J.V. Barth and K. Kern : Surface-templated assembly of 2D metal-organic coordination networks, **J. Phys. Chem. B 110**, 23472 (2006).
8. M.E. Cañas-Ventura, F. Klappenberger, S. Clair, S. Pons, K. Kern, H. Brune, T. Strunskus, Ch. Wöll, R. Fasel and J.V. Barth : Coexistence of one- and two-dimensional supramolecular assemblies of terephthalic acid on Pd(111) due to self-limiting deprotonation, **J. Chem. Phys. 125**, 184710 (2006).
9. A. Dmitriev, A.P. Seitsonen, H. Spillmann, N. Lin, T. Strunskus, Ch. Wöll, J.V. Barth, K. Kern : Asymmetry induction by cooperative intermolecular hydrogen bonds in surface-anchored layers of achiral molecules, **ChemPhysChem 7**, 2197 - 2204 (2006).
10. S. Stepanow, N. Lin, J.V. Barth and K. Kern: Non-covalent binding of fullerenes and biomolecules at surface-supported metallosupramolecular receptors, **Chem. Comm.** 2153 - 2155 (2006).
11. A.P. Seitsonen, M. Lingenfelder, H. Spillmann, A. Dmitriev, S. Stepanow, N. Lin, K. Kern and J.V. Barth : Density functional theory analysis of carboxylate-bridged di-iron units in two-dimensional metal-organic grids, **J. Am. Chem. Soc. 128**, 5634 – 5635 (2006).
12. S. Clair, S. Pons, S. Fabris, S. Baroni, H. Brune, K. Kern and J.V. Barth : Monitoring two-dimensional coordination reactions: directed assembly of Co-terephthalate nanosystems on Au(111), **J. Phys. Chem. B 110**, 5627 - 5632 (2006).
13. "Multiple Length Scale Patterning of Single-Molecule Magnets"

M. Cavallini, F. Biscarini, J. Gómez-Segura, D. Ruiz, J. Veciana.

Nano Lett., **2003**, *3***,** 1527-1530.

14. "*Magnetic Information Storage on Polymers Using Patterned Single-Molecule Magnets"*

M. Cavallini, J. Gómez-Segura, D. Ruiz-Molina, M. Massi, C. Albonetti, C. Rovira. J. Veciana, F. Biscarini *Angew. Chem. Int. Ed.,* **2005**, *44*, 888-892.

15. "Ordered patterning of nanometric rings of single molecule magnets on polymers by Lithographic spatial control of demixing" M. Cavallini, J. Gomez-Segura, C. Albonetti, D. Ruiz, J. Veciana, F. Biscarini.

J. Phys. Chem, B, **2006**, *110*, 11608-11610 (2006)

16.“Self-Assembled Monolayers of a Multifunctional Organic Radical”
N. Crivillers, M. Mas-Torrent, S. Perruchas, J. Vidal-Gancedo, J. Veciana, C. Rovira, L. Basabe-Desmonts, B. Jan Ravoo, M. Crego-Calama, D.N. Reinhoudt.
Angew. Chem. Int. Ed., **2007**, *46*, 2215-2219.

15. N. Lin, S. Stepanow, F. Vidal, K. Kern, S. Alam, S. Strömsdörfer, S. Dremov, P. Müller, A. Landa and M. Ruben, Surface-assisted coordination chemistry and self-assembly, Dalton Trans., 2794 (2006)

16. M. Ruben, D. Payer, A. Landa, A. Comisso, C. Gattinoni, N. Lin, J.-P. Collin, J.-P. Sauvage, A. De Vita, and K. Kern, 2D supramolecular assemblies of Benzene 1,3,5-tri-yl Tribenzoic Acid: Temperature-induced phase transformations and hierarchical organization with macrocyclic molecules, J. Am. Chem. Soc. 128, 15644 (2006)

17. M. Lingenfelder, G. Tomba, G. Costantini, L. Colombi Ciacchi, A. De Vita, and K. Kern, Tracking the Chiral Recognition of Adsorbed Dipeptides at the Single Molecule Level, Angew. Chem. Int. Ed., in press (2007)

18. D. Payer, A. Comisso, A. Dmitriev, T. Strunkskus, N. Lin, C. Wöll, A. DeVita, J.V. Barth, and K. Kern, Ionic hydrogen bonds controlling 2-dimensional supramolecular systems at metal surfaces, Chem. Eur. J. 13, 3900 (2007)

19. W. Xu, M. Dong, H. Gersen, S. Vázquez-Campos, E. Lægsgaard, I. Stensgaard, M. Crego-Calama, D. N. Reinhoudt, T. R. Linderoth, and F. Besenbacher
Enhanced Stability of Large Molecules Vacuum-Sublimated onto Au(111) Achieved by Incorporation of Coordinated Au-AtomsSubmitted (2007).

20. S. Vázquez-Campos, M. Péter, M. Dong, S. Xu, W. Xu, H. Gersen, T.R. Linderoth, H. Schönherr, F. Besenbacher, M. Crego-Calama, D. N. Reinhoudt
Self-Organization of Gold-Containing Hydrogen-Bonded Rosette Assemblies on Graphite Surface. submitted (2007**)**

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

21. J.V. Barth : Molecular architectonic on metal surfaces, **Annu. Rev. Phys. Chem. 58**, 375 – 407 (2007).

22. W. Auwärter, F. Klappenberger, A. Weber-Bargioni, A. Schiffrin, Y. Pennec, T. Strunskus, Ch. Wöll and J.V. Barth : Adsorption induced deformation and selective adatom capturing of tetrapyridyl-porphyrin molecules on a copper (111) surface, subm.

23. *"Advances on the nanostructuration of functional molecules on surfaces: The case of Single-Molecule Magnets (SMM)"*
J. Gómez-Segura, J. Veciana, D. Ruiz-Molina.
Chem. Commun., DOI: 10.1039/b616352a, 2007.

24. "New insights into ligand inductive effects on the stability of Mn12 single molecule magnets. Synthesis, magnetic and thermal characterization of complex $[Mn_{12}O_{12}(O_2CC.CH)_{16}(H_2O)^4]\cdot 3H_2O$ and the corresponding manganese(II) propiolate $[Mn_3(O_2CC.CH)_6(H_2O)_4]\cdot 2H_2O$ derived by thermolysis reaction".
Dalton Trans., **DOI:** 10.1039/b700298j, 2007. J. Gómez-Segura, J. Campo, I. Imaz, K. Wurst, J. Veciana, Ph. Gerbier, D. Ruiz-Molina.

25. R. Otero, F. Rosei, Y. Naitoh, P. Jiang, P. Thostrup, A. Gourdon, E. Lægsgaard, I. Stensgaard, C. Joachim and F. Besenbacher, Nanostructuring Cu Surfaces Using Custom-Designed Molecular Molds, Nano Letters **4** (2004) 75

25. R. Otero, Y. Naitoh, F. Rosei, P. Jiang, P. Thostrup, A. Gourdon, E. Lægsgaard, I. Stensgaard, C. Joachim and F. Besenbacher, One-dimensional assembly and selective orientation of lander molecules on an O-Cu template, Angew. Chem. Int. Ed. **16** (2004) 2092

26. Kühnle, L. Molina, T. Linderoth, B. Hammer, and F. Besenbacher, Growth of unidirectional molecular rows of cysteine on Au(110)-(1x2) driven by adsorbate-induced surface rearrangements, Phys. Rev. Letters **93** (2004) 086101

27. R. Otero, F. Hümmelink, F. Sato, S.B. Legoas, P. Thostrup,, E. Lægsgaard, D.S. Galvão, I. Stensgaard, and F. Besenbacher, Lock-and-key effect in the surface diffusion of large organic molecules probed by STM, Nature Materials, Nature Materials **3** (2004) 779

28. R. Otero, M. Schöck, L.M. Molina, E. Lægsgaard, I. Stensgaard, B. Hammer, and F. Besenbacher, Guanine quartet networks stabilized by cooperative hydrogen bonds, Angewandte Chemie **44** (2005) 2270

29. Kühnle, T.R. Linderoth, M. Schunack and F. Besenbacher, L-Cysteine Adsorption Structures on Au(111) Investigated by Scanning Tunneling Microscopy under Ultrahigh Vacuum Conditions, Langmuir **22** (2005) 2156-2160

30. S. Weigelt, C. Busse, L. Petersen, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher og T. R. Linderoth, Chiral switching by spontaneous conformational change in adsorbed organic molecules, Nature Materials **5** (2006) 112-117

31. J.A. Miwa, S. Weigelt, H. Gersen, F. Besenbacher, F. Rosei and T. Linderoth, Azobenzene on Cu(110): adsorption site-dependent diffusion, J. Am. Chem. Soc. **128** (2006) 3164-3165

32. S. Xu, M.Dong, E. Rauls, R.Otero, T.R. Linderoth and F. Besenbacher, Co-adsorption of Guanine and Cytosine on Graphite: Ordered Structure Based on GC Pairing, Nano Letters **6** (7) (2006) 1434-1438, 10.1021/nl060563u

33. M. Schöck, R. Otero, S. Stojkovic, F. Hümmelink, A. Gourdon, E. Lægsgaard, I. Stensgaard, C. Joachim and F. Besenbacher, Chiral close-packing of achiral star-shaped molecules on solid surfaces, Journal of Physical Chemistry Letters B **110** (2006) 12835-12838, 10.1021/jp0619437

34. W. Xu, M. Dong, H. Gersen, E. Rauls, S. Vazquez-Campos, M. Crego-Calama, D. N. Reinhoudt, I. Stensgaard, E. Laegsgaard, T. R. Linderoth, and F. Besenbacher
Cyanuric Acid and Melamine on Au(111): Structure and Energetics of Hydrogen-Bonded Networks, SMALL, **3** 854 (2007)

35. C. Busse, S. Weigelt, L. Petersen, A. H. Thomsen, M. Nielsen, K. V. Gothelf, E. Lægsgaard, F. Besenbacher, and T. R. Linderoth
Chiral ordering and conformational dynamics for a class of oligo-phenylene-ethynylenes on Au(111), Journ. Phys. Chem. C, accepted (2007)

36. S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, T. Strunskus, C. Wöll, M. Dahlbom, B. Hammer, E. Lægsgaard, F. Besenbacher, and T. R. Linderoth
Covalently bound molecular nanostructures by organic chemistry in two dimensions. submitted (2007)

37. G.Moras, G.Csanyi, M.C.Payne, A. De Vita, "A novel molecular dynamics approach to large semiconductor systems", Physica B 376, 936 (2006).

38. G.Csanyi, G.Moras, J.R.Kermode, M.C.Payne A.Mainwood and A.DeVita, in "Theory of Defects in Semiconductors", Springer series: Topics in Applied Physics, D.A.Drabold and S.Estreicher eds.Vol.104,193(2007).

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

1. *'Ordered molecular nanoarrays'*, Highlight in **Chemical Science** June 2006, Issue 6, C45.
2. *'Networking with odd numbers'*, Research news in **Nanotoday**, Feb 2007, Vol2 2, No 11, 10.

1 D. Patents and industry collaborations

1. *"Metodo per la realizzazione di un film sottile di composizione chimica spazialmente strutturata su scala micrometrica o nanometrica su un supporto".*
   M. Cavallini, F. Biscarini, D. Ruiz-Molina, J. Gómez Segura, J. Veciana.
   Patent: BO2004A000076. Date: 17/02/2004. PCT/EP05/001494
   Patent licenced to the italian SME *NanoScribba*.

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

March 2006: Organsation of the Kloster Irsee Meeting

1 F. Participation in other conferences

Please list only the most relevant

A. Invited talks :

1. *Supramolecular engineering on metal surfaces*, New Materials at the Nanometric Scale, European Interreg. Workshop, Trieste (Italy), 23 – 24 oct. 2006. [J.V. Barth]
2. *Supramolecular engineering on metal surfaces*, Microscience 2006 & UK SPM meeting, London (UK), 27 – 29 june 2006. [J.V. Barth]

3. *Steering molecular organization on surfaces*, EU Network of Excellence workshop - Organizing and addressing molecules at surfaces, Playa de Aro (Spain), 24 – 28 may 2006. [J.V. Barth]

B. Conference Contributions :

4. F. Klappenberger, M.E. Cañas-Ventura, S. Clair, S. Pons, U. Schlickum, K. Kern, H. Brune, Z.-R. Qu, M. Ruben, T. Strunskus, Ch. Wöll, A. Comisso, A. DeVita, J.V. Barth: *Multiconfigurational ordering of a diphenyl oxalamide on thereconstructed Au(111) surface*, ICN&T, Basel (Switzerland), 30 July - 4 August 2006.
5. M.E. Cañas-Ventura, F. Klappenberger, S. Clair, S. Pons, K. Kern, H. Brune, T. Strunskus, Ch. Wöll, R. Fasel and J.V. Barth: *Surface chemical bonding, and coexisting one-dimensional chaining and two-dimensional islanding of a ditopic carboxylic acid linker molecule on Pd(111)*, ECOSS, Paris (France), 4 – 8 sept. 2006.
6. W. Auwärter and J.V. Barth *Supramolecular engineering on metal surfaces :* mol|CH|surf discussion meeting, Bern (Switzerland), 12 july 2006.
7. F. Klappenberger, M.E. Cañas-Ventura, S. Clair, S. Pons, U. Schlickum, K. Kern, H. Brune, Z.-R. Qu, M. Ruben, T. Strunskus, Ch. Wöll, A. Comisso, A. DeVita, J.V. Barth: *Supramolecular ordering of an oxalic amide derivate on Au(111) studied by STM and NEXAFS*, ECOSS, Paris (France), 4 – 8 sept. 2006.
8. U. Schlickum, F. Klappenberger, M.E. Cañas-Ventura, S. Pons, S. Clair, K. Kern, Z.R. Qu, M. Ruben, R. Fasel, H. Brune, J.V. Barth : *Self-assambly of oxalic amid molecules on the reconstructed Au (111) surface*, Workshop Functional Molecular Nanostructures, Kloster Irsee (Germany), 26 – 29 april 2006.
9. U. Schlickum, F. Klappenberger, K. Kern, G. Zoppellaro, M. Ruben, H. Brune, J.V. Barth : *Cobalt directed assembly of cyanophenyl linker molecules*, ESF conference on Self-organized Nanostructures (SONS), Pisa, (Italy), 29 june – 1 july 2006.
10. U. Schlickum, R. Decker, F. Klappenberger, G. Zoppellaro, M. Ruben, K. Kern, H. Brune, J.V. Barth : *Three-fold coordinated metal organic honeycomb network*, Spin-Polarized Currents in Magnetic Nanostructures, Bad Honnef, (Germany), 3 – 5 jan. 2007.

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

Christian Bombis, Post.doc.	01.12.05-31.01.06	
Mats Dahlbom, Post.doc.	01.08.05-14.06.06	
Jianguo Wang, Post.doc.	01.01.06-13.09.06	
Uta Schlickum, Post.doc.	01.01.06-30.10.06	
Chandru Rajdurai, Post.doc.	01.01.06-31.12.06	
Sebastian Stepanow, PhD,	01.01.06-31.12.06	(November 2005)
Alessio Comisso, PhD,	01.01.06-31.12.06	(March 2007)

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"NEDSPE–Nanoscale electronic devices via templating supramolecular polyelectrolytes'

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number ():02-PE-SONS-092-NEDSPE Acronym / Short Title: NEDSPE Full Title: Nanoscale electronic devices via templating supramolecular polyelectrolytes Project Leader name: *Prof. Dr. Manferd Stamm* Project Leader affiliation: *Department of Physical Chemistry and physics of Polymers, Leibniz-Institut fur Polymerforschung, Dresden, Germany, (IPF) and Tecnische Universitat Dresden (TUD)* Institutional home page (URL): *www.ipfdd.de* Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator (name & affiliation): Dr Manfred Stamm, Prof. of Physical Chemistry of Polymeric Materials, Department of Physical Chemistrt and Physics of Polymers, Leibniz-Institut fur Polymerforschung, Dresden (IPF) and Technische Universitat, Dresden (TUD), Str. 6, 01069 Dresden, Germany
Total Funding amount of the IP *(to be corrected by the PI) €128.038*
IP 2
Principal Investigator (name & affiliation): Prof. Dr. Robert Jerome, Centre d'Etude et de Recherce sur les Macromolecules (CERM), Universite' de Liege, Sart-Tilman, B6a, 4000 Liege, Belgique.
Total Funding amount of the IP *(to be corrected by the PI)* € *41387*

IP 3
Principal Investigator (name & affiliation): Dr. Vojislav Krstic, Laboratoire Nationale des Champs Magnetique Pulses, CNRS (LNCMP), 143 Av. De Rangueil, 31432 Toulouse Cedex 4, France
Total Funding amount of the IP (to be corrected by the PI) 0€

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

During the work under SONS-project we developed general methods to handle single polyelectrolyte molecules: immobilization, imaging, manipulation, deposition of some desired materials (both inorganic and organic) selectively along polyelectrolyte molecules. These achievements were a basis for construction of simplest devices. In the previous account we reported our preliminary results of synthesis and characterization of polypyrrole (Ppy) nanofibers polymerised from individual polyanion molecules stretched between electrodes. We demonstrated that they are electrically conductive and that the conductivity indeed cams from single fibers. We also reported modification of multiwalled carbon nanotubes with polymer brushes that made them easily dispersible in water and gave a possibility of further modifications of their surfaces on a desired fashion. Finally, we employed the dispersion of P2VP-modified CNTs produced by the **CERM** group for a preparation of thin coatings which appeared to be highly conductive and moderately transparent.

Being highly experienced and qualified specialist in polymer synthesis the **CERM** group has provided the CRP with necessary samples of polymers, which then were used by IPF group as a templates for synthesis of the desired nanostructures and further characterized together with the **LNCMP** group (for details, see the corresponding paragraphs of the IPs).

The synthesis of high molecular weight “hairy” polyelectrolytes and polyelectrolytes with pendant pyrrole groups on each monomer unit was performed (**CERM)** and these molecules were explored as templates for nanowires (**IPF**).

2) The general method to (ultimately) stretch single polycation molecules (**CERM)** via codeposition
with octylamine and then to measure their length and determine their molecular weight (**IPF**).

3) The preparation procedure of the Ppy nanofibers was optimised (**CERM, IPF)**.

4) An extended electrical characterization of the Ppy nanofibers was performed **(IPF and LNCMP)**. This includes investigations of the temperature dependence of the conductivity, characterization of the nanofibers in the dry state and under water solutions of different pH and doping levels **(IPF and LNCMP)**. As expected for conductive polymers, we found that the conductivity of single fibers can be modulated by changing of the environment and, as the result, altering of the doping level. Furthermore, even at relatively high ionic strength of solution (0.1M) the conductivity through the individual slightly doped Ppy fibers exceeds well the background conductivity through the solution. These facts are very promising for construction of bio- and chemical sensors on the basis of Ppy nanofibers.

5) Additional samples of carbon nanotubes grafted with P2VP chains (CNT-g-P2VP) were prepared (**CERM)** and were successfully used for the preparation of transparent and conducting CNTs films **(IPF)**.

6) A new approach for the functionalization of CNTs with carboxylic groups were proposed. The adsorption of Fe_3O_4 nanoparticles onto their surface lead to magnetic CNTs which could be oriented in a magnetic field (**CERM)**.

Keywords: *Single polymer molecules, conductive polymer nanowire, polyelectrolytes, anionic polymerization, magnetic nanoparticles, carbon nanotubes*

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

Mostly, we are going along the tasks written in the proposal. We, however, have to admit, that the study of modified carbon nanotubes was not initially among the focus of the proposal. Nevertheless, it is an additional activity, which is related to the main focus of the project and which in our opinion provides a valuable extension of the main project tasks.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

The EUROCORES programme gives a valuable opportunity to work on a joint project with European partners. This is an extremely useful funding instrument with relatively little administrative overhead and should be used to encourage further development of this area of self-organised nanostructures which has been started in SONS1 and SONS2. It is noticeable that much of the currently funded work is in polymeric materials and it could be valuable to re-balance the portfolio of work with more on hierarchical inorganic materials, and area where there is also currently much interesting research activity. Possibly two programmes are needed (one for polymeric materials, one for inorganic materials) but personally I believe that the two fields would benefit from more cross-fertilization of the sort which is specifically encouraged in the EUROCORES programmes via the workshops and interaction over several CRPs as well as within the CRPs. The ability to carry out fundamental research in these programmes as well as nearer application work is also a valuable feature of the programme.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

The SONS program of the European Science Foundation has proven to be an excellent starting point for highest quality fundamental research. It encourages the continuation of the research in the field of the project in particular, and also on a wider scientific ground, after the official project termination. Furthermore, the program allowed principally for an easier collaboration between the project partners, but also with groups outside the project which showed interest in the work performed within the program. Therefore, future networks on the research field covered by the SONS program will arise.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

The main results were published in the following papers:

1. V. Bocharova, A. Kiriy, M. Stamm, F. Stoffelbach, R. Jérôme, C. Detrembleur. Simple Method for Stretching and Alignment of Single Adsorbed Synthetic Polycation molecules. *Small* **2006**, *2*, 910-916.

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2. Bocharova, V.; Kiriy, A.; Oertel,U.; Stamm, M.; Stoffelbach,F.; Detrembleur, C.; Jérôme, R. Ultrathin Conductive Transparent Films of Modified Multi-Walled Carbon Nanotubes. *J. Phys. Chem. B.* **2006,** *110*, 14640-14644.

3. A. Kiriy, J. Yu, M. Stamm. Interpolyelectrolyte Complexes: A Single-Molecule Insight. *Langmuir* **2006**, *22*, 1800-1803.

4. Bocharova, V.; Gorodyska, G.; Kiriy, A.; Stamm, M.; Simon, P.; Mönch, I.; Elefant, D.; Lou, X.; Stoffelbach, F.; Detrembleur, C.; Jérôme, R. Facile Synthesis and Arrangement of Water-Dispersible Prussian Blue Nanocrystals. In: Characterization of Polymer Surfaces and Thin Films Series: *Progress in Colloid and Polymer Science* Vol. 132 Grundke, K.; Stamm, M.; Adler, H.-J. (Eds.) **2006**, ISBN: 3-540-31241-2.

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

The main results were published in the following papers:

1. V. Bocharova, A. Kiriy, M. Stamm, F. Stoffelbach, R. Jérôme, C. Detrembleur. Simple Method for Stretching and Alignment of Single Adsorbed Synthetic Polycation molecules. *Small* **2006**, *2*, 910-916.

SONS: 01/07/2008 3 / 34

2. Bocharova, V.; Kiriy, A.; Oertel,U.; Stamm, M.; Stoffelbach,F.; Detrembleur, C.; Jérôme, R. Ultrathin Conductive Transparent Films of Modified Multi-Walled Carbon Nanotubes. *J. Phys. Chem. B.* **2006,** *110*, 14640-14644.

3. A. Kiriy, J. Yu, M. Stamm. Interpolyelectrolyte Complexes: A Single-Molecule Insight. *Langmuir* **2006**, *22*, 1800-1803.

4. Bocharova, V.; Gorodyska, G.; Kiriy, A.; Stamm, M.; Simon, P.; Mönch, I.; Elefant, D.; Lou, X.; Stoffelbach, F.; Detrembleur, C.; Jérôme, R. Facile Synthesis and Arrangement of Water-Dispersible Prussian Blue Nanocrystals. In: Characterization of Polymer Surfaces and Thin Films Series: *Progress in Colloid and Polymer Science* Vol. 132 Grundke, K.; Stamm, M.; Adler, H.-J. (Eds.) **2006**, ISBN: 3-540-31241-2.

5. Kiriy, A.; Bocharova, V.; Gorodyska, G.; Simon, P.; Mönch, I.; Elefant, D.; Stamm, M. Assembling of Prussian Blue Nanoclusters Along Single Polyelectrolyte Molecules. In Metal-Containing and Metallo-Supramolecular Polymers and Materials *(ACS Symposium Series 928)* Schubert U.; Newkome, G.; Manner, G.; Eds.; American Chemical Society (Oxford University Press): Washington, **2006**, pp 500-513.

6. Bocharova, V.; Kiriy, A.; Vinzelberg, H.; Mönch, I.; Stamm, M. Polypyrrole Nanowires Grown from Single Adsorbed Polyelectrolyte Molecules. *Angewandte Chemie* **2005**, *117*, 6549-6552.

7. Kiriy, A.; Gorodyska, G.; Kiriy, N.; Separovich, R.; Lupisky, R.; Minko, S.; Stamm, M. AFM Imaging of Single Polycation Molecules Contrasted with Cyanide-Bridged Compounds *Macromolecules* **2005**, *38*, 501-506.

8. Lou, X.; Detrembleur, C.; Pagnoulle, C.; Jérôme, R.;* Bocharova, V.; Kiriy, A.; Stamm, M. Surface Modification of Multi-Walled Carbon Nanotubes by Poly(2-Vinylpyridine): Dispersion, Selective Deposition and Decoration of the Nanotubes. *Adv. Mater.* **2004**, *16*, 2123-2127.

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

1 D. Patents and industry collaborations

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

- Active and permanent exchange of the scientific information and samples between the partners.
- Project meeting connected with workshop on **"Self-assembled structures of amphiphilic ionic copolymers**", convened by Dr. Olivier Diat, Oleg Borisov and Günter Reiter, Arcachon, France, 11-14 May 2005

1 F. Participation in other conferences

Please list only the most relevant

ACS 2005
European Polymer Congress 2005 in Moscow.

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

IPF: Vera Bocharova, PhD-student, 1.10.03-31.12.2006
CERM: Dr. François Stoffelbach, post-doc, 01.01.2004-31.12.2006
Christophe Hubens, technician, 01.01.2004-31.12.2006
LNCMP: Viktor Siegle, PhD-student, 1.01.2004-31.12.2006

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number ():02-PE-SONS-112 Acronym / Short Title: AMPHI Full Title: Self-Organized Amphiphilic Block Copolymer Nanostructures Project Leader name: Petr Stepánek Project Leader affiliation: Institute of Macromolecular Chemistry, Prague, Czech Republic Institutional home page (URL): www.imc.cas.cz Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP1
Principal Investigator (name & affiliation): Petr Stepanek, Institute of Macromolecular Chemistry, Prague, Czech Republic
Total Funding amount of the IP *(to be corrected by the PI)* 2948000 CZK, about 105000 Euro
IP 2
Principal Investigator (name & affiliation): Olivier Diat, UMR 5819 SPrAM, CEA-Grenoble
Total Funding amount of the IP *(to be corrected by the PI)*
AP 1
Principal Investigator (name & affiliation): Prof. Frédéric Nallet, CRPP-CNRS, Pessac, France

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

Several types of diblock copolymers intended as model polymers for producing membranes with ordered structure have been synthesized. The aim is to create membranes with ordered structure that at the same time would exhibit conductivity properties appropriate for application in fuel cells. Many samples of polymers have been prepared at IMC of these general types: sulfonated polystyrene-*block*-poly(ethylene propylene) diblock copolymers, polystyrene-*block*-poly(2-dimethylaminoethyl methacrylate) copolymers, polystyrene-*block*-poly(styrene-*co*-acrylonitrile) copolymers, quaternized copolymers of poly(styrene-*block*-4-vinylpyridine), graft copolymers formed of a poly(styrene-co-chloromethylstyrene) backbone and poly(t-butylacrylate) grafts, linked to a polystyrene second block.

These polymers fulfill the requirements that they contain either proton conductive groups (sulfonic function) or OH^- conductive groups (amino groups). In addition, the acrylonitrile containing polymers were tetrazolated and can be further converted to both proton conductive units by acid doping or be made anion conductive by quaternization. Solution properties of these materials have been investigated by dynamic light scattering. Understanding solution behavior is essential, since membranes are cast from polymer solutions and the structure of polymer in solution is reflected in the properties of the membrane. Various degrees of clustering have been observed as a function of the content of the ionogenic component in these systems. Bulk and membrane properties of these systems have been observed by small-angle X-ray scattering, atomic force microscopy, conductometry and in some cases also by small-angle neutron scattering.

The post-functionalization of a previously synthesized diblock or triblock copolymer systems is less elegant than the direct construction of ionic system but it is an easier method to develop compared to imagining new routes of synthesis with ionic copolymers. This is justified in this case because the ionic segregation will exist by construction of the block separation.

In parallel, studies of existing proton conductive materials have been conducted, in particular Nafion.

We have determined the type and conditions of sulfonation reaction that lead to stable reproducible results. We have determined the aggregation behavior of the sulfonated polymers. We have shown that clusters of the more sulfonated material form during the membrane preparation process that persists in the finished membranes. We have determined the structural and morphological properties of these membranes. We have determined the swelling of these membranes and conductivity as a function of the sulfonation degree. We have shown that local swelling of the conductive clusters of the membranes van be conveniently studies by atomic force microscopy.

We have synthesized several types of OH^- conducting ionomers. We have prepared, to various degrees of quaternization, polymers of polystyrene-polyvinylpyridine and polystyrene-*block*-poly(2-dimethylaminoethyl methacrylate). In order to decrease the brittleness of these polymers we have prepared these polymers also with plasticizers. These were either additive plasticizers, such as dioctylphthalate or built-in plasticizers, in particular isoprene monomers covalently bound in the polystyrene block of the copolymer. We have also succeeded in preparing an OH^- conducting polymer based on a diblock copolymer of polystyrene-polyacrylonitrile. The latter

block in this polymer had first to be transformed into a polyvinyltetrazole, which was subsequently quaternized. Structural and morphological properties of these polymers were determined using X-ray scattering, atomic force microscopy and transmission electron microscopy.
For the hydrated Nafion materials it was shown that they consist of fibrillar structure made of elongated polymeric aggregates surrounded with ionic charges. Conductivity and transport measurements on sulfonated polyimide membranes show that they consist of a multiscale foliated structure.
Thus we have reached the project objectives in preparing a number of block copolymer systems that can be used as models for preparation of self-organized materials applicable in fuel cell design, and we have described their structural and conductivity properties.
A certain difficulty appeared when we moved to obtaining large films with the suitable physical properties (high ionic conductivity and good mechanical properties) with a large variation of response in order to quantify the relationship between structure and ionic transport. The increase of ionic functions has a negative influence on the mechanical properties due to the weak molecular weight, necessary for a strong and local phase separation in these block copolymers. These two requirements have opposite effect.
Then, a strong effort in these two last years was to understand the local mobility of the confined ion is these soft structures as function of temperature and water content and to characterize the effect of host particles that can improve the mechanical properties as well as the ionic conduction at low water content.

All these results could not be achieved without the collaboration within this CRP. Indeed this was efficiently combining the expertise of the group at CEA in fuel cell materials, the expertise of the group at IMC in polymer synthesis and characterization and the expertise of the partners at CRPP in structure investigation. The combination of these inputs ensured a consistent approach and generated new directions in our efforts in this field of research. Thus we have decided to extend the investigated materials to anion conductive polymers, as explained above, and to plasticized membrane materials, as explained below.

We have also been aware of an intense interest of other research groups within the SONS program in applications of amphiphilic copolymers, which initiated the organization of two workshops by this CRP, namely “Self-assembled structures of amphiphilic ionic copolymers in solutions and at interfaces”, 11-14 May 2005, Arcachon (France) organized by Olivier Diat and colleagues, and “Structure and properties of self-organized amphiphilic copolymers”, 4–7 October 2006, Prague (Czech Republic), organized by Petr Stepanek and colleagues.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

The main difficulty is to obtain flexible and homogeneous (in density and thickness) membranes in order to perform several tests for structure and transport analysis. Indeed, it is important to vary different parameters such as the water content, the ion content to be able to model this type of self-assembled ionic systems.
To be able to work with small quantities of membrane materials, we have built a humidity cell in which the water partial pressure can be continuously varied. This cell allows us to analyze the water content on the same sample using x-ray scattering technique and without manipulation. However, the water sorption equilibrium time is long and beam time consuming which is not really suitable for synchrotron experiments. An automatization at the CEA laboratory is in progress to be able to work using a rotating anode x-ray source.
The mechanical features are quite important for this project and can be improved using a

plastifiant. The plastifiant can be either a low-molecular weight additive or it can be a soft comonomer copolymerized in the polymer itself. Polymers containing isoprene and octylstyrene have been synthesized and their properties are being evaluated. However, the plastifiant then becomes another unknown variable in the structural understanding, which is already not trivial, since the material then contains four components – the two incompatible monomers, the functionalized monomer and the plastifiant.
One way, which has not been enough explored and that can be promising, is to work more on the polymer solution conformation before the casting process through which the system is quenched in a metastable state. Since the different blocks are soluble in different solvents, temperature remains a suitable variable to control the phase separation in these systems.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

Two of the present partners are involved in a new Eurocores project BIOSONS within the SONS II call: the group at IMC (project leader P. Stepanek) as IP3 and the group at CRPP (project leader F. Nallet) as Cooperating Partner.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

The subject of self-organized materials is still very 'hot' and directly related to the current growth, expansion and world-wide efforts in nanotechnologies, both in technical and in bio-related applications. ESF and Eurocores should in my opinion continue in supporting these activities by, e.g., organizing a SONS III program

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

This is an excellent instrument for promoting collaboration in European research by providing opportunities of collaboration not only to the scientific groups involved but also to funding agencies. The administrative and organizational issues of the Eurocores programme are lighter then in certain European projects which doubtlessly is an attractive feature. The added value is in the fact that European cooperation is involved in research that is financed by national agencies. Therefore a different quality of deliverables can be obtained for a given financial effort of the funding agencies. For the research teams involved, interaction with European partners working in the similar fields of activity is very stimulating.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The only difficulty might be the need for double reporting on the same activities to national agencies on one side and to ESF on the other side, but this has largely been improved by this present new ESF reporting scheme.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

Daniel Gromadzki, Peter Cernoch, Miroslav Janata, Vlastimilo Kudela, Frédéric Nallet, Olivier Diat, Petr Stepánek
« Sulfonated polystyrene-block-hydrogenated polyisoprene ionomers. II. Morphological studies and ionic transport properties of partially sulfonated diblock copolymers »
Eur. Polym. J. , 42 (10) (2006) 2486-96

Janata M., Kedela V., Gromadzki D., Peter Cernoch, Stepánek P., Nallet, F., Diat O., Vlcek P. and Toman L.
« Synthesis of highly sulfonated polystyrene-based block copolymers soluble in tetrahydrofuran »
E-Polymers, 55 (2006)

Daniel Gromadzki, Jan Lokaj, Peter Černoch, Olivier Diat, Frédéric Nallet, Petr Štěpánek
The structure of polystyrene-*block*-poly(styrene-*co*-acrylonitrile) and polystyrene-*block*-poly(styrene-*co*-acrylonitrile-5-vinyltetrazole) diblock copolymers prepared by Nitroxide-Mediated Radical Polymerization and "Click Chemistry"
Eur. Polym. J., submitted

Lokaj J., Poláková L., Holler P., Starovoytova L., Štěpánek P., Diat O.
Diblock copolymers comprising poly(2-vinylpyridine-co-acrylonitrile) and polystyrene blocks by nitroxide-mediated radical polymerization
J. Appl. Polym. Sci., accepted

Small-angle neutron scattering from solutions of diblock copolymers in partially miscible solvents
P. Štěpánek, Z. Tuzar, F. Nallet, L. Noirez,
Macromolecules, 38, 3426, 2005

Štěpánek P., Černoch P., Tuzar Z., Nallet F., Diat O., Self-organized nanostructures in multicomponent polymer systems: structure and dynamic properties, 41st World Polymer Congress 'Macro', Abstracts, p. 101, Rio de Janeiro 2006

Lokaj J., Poláková L., Holler P., Štěpánek P., Diat O., Chain extension of nitroxide-terminated polymer macroinitiators with 2-(dimethylamino)ethyl methacrylate, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract PC 35, p. 100

Lokaj J., Poláková L., Holler P., Štěpánek P., Diat O., Block polyelectrolytes containing quaternized 2-(dimethylamino)ethyl methacrylate units, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract PC 34, p. 99

Poláková L., Lokaj J., Štěpánek P., Diat O., Nitroxide-terminated polymer macroinitiators and related functional block copolymers, Self-organized Nanostructures (SONS) Conference, Pisa 2006, Abstracts, unpaged

Štěpánek P., Tuzar Z., Černoch P., Nallet F., Diat O., Self-organized nanostructures in

multicomponent polymer systems: structure and dynamic properties, Self-organized Nanostructures (SONS) Conference, Pisa 2006, Abstracts, unpaged

Černoch P., Janata M., Štěpánek P., Nallet F., Self-organization of block copolymers in bulk and in thin films, Self-organized Nanostructures (SONS) Conference, Pisa 2006, Abstracts, unpaged

Štěpánek P., Tuzar Z., Černoch P., Nallet F., Noirez L., Self-oganized nanostructures in multicomponent polymer systems, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract SL 22, p. 62

Gromadzki D., Černoch P., Janata M., Kůdela V., Nallet F., Diat O., Štěpánek P., Morphological studies and ionic transport properties of partially sulfonated diblock copolymers, SONS Conference on Self-organized Nanostructures, Pisa 2006, Book of Abstracts, P29

Tuzar Z., Štěpánek P., Ryukhtin V., Kadlec P., Nallet F., Noirez L., Structure and dynamics of block copolymers in partially miscible solvents: SANS and DLS study, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract PC 67, p. 132

Gromadzki D., Černoch P., Janata M., Kůdela V., Nallet F., Diat O., Štěpánek P. , Structure and transport properties of partially sulfonated diblock copolymers, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract PC 66, p. 131

Poláková L., Lokaj J., Holler P., Starovoytova L., Štěpánek P., Diat O., Copolymers containing 4/vinylpyridine, acrylonitrile and styrene units by controlled radical polymerization, SONS Networking Activity Workshop ' Structure and properties of self-organized amphiphilic copolymers'Prague 2006

Lokaj J., Poláková L., Holler P., Starovoytova L., Štěpánek P., Diat O., Diblock copolymers cocomprising poly(2-vinylpyridine-co-acrylonitrile) and polystyrene blocks by nitroxide-mediated radical polymerization, SONS Networking Activity Workshop ' Structure and properties of self-organized amphiphilic copolymers'Prague 2006

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

Diat, O. et G. Gebel
"Block-ionomer for fuel cell application", chapter 9 in « Block Copolymers in Nanoscience, Edited by Lazzari, Liu & Lecommandoux, 2006, Published by WILEY-VCH

Surface patterns of block copolymers in thin layers after vapor treatment
Peter Černoch , Petr Štěpánek, Josef Pleštil, Miroslav Šlouf, Alexander Sidorenko, Manfred Stamm
Eur.Pol.J., accepted

O. Diat, Gebel G. and M. Pineri.
« Water desorbtion in Nafion membrane as a function of temperature »
J. Memb. Sci. submitted

J.Teisseire, F. Nallet, P.Fabre and C. Gay, Understanding cracking versus cavitation in pressure-sensitive adhesive: The role of kinetics, *J. Adhesion*, accepted (2007)

C. Faure, F. Nallet, D. Roux, S. Milner, F. Gauffre, D. Oléa and O. Lambert, Modeling leakage kinetics from multilamellar vesicles for membrane permeability determination: application to glucose, *Biophys. J.,* 91, 12, 4340-4349, (2006)

P. Fernandes, P. Barois, E. Grelet, F. Nallet, J.W. Goodby, M. Hird and J-S. Micha, Extension of the resonant scattering technique to liquid crystals without resonant element, *Eur. Phys. J. E.,* 20, 81-87, (2006)

P. Moreau, L. Navailles, J. Giermanska-Kahn, O. Mondain-Monval, F. Nallet and D. Roux, Dislocation-loop-mediated smectic melting, *Europhys. Lett.,* 73, 1, 49-54, (2006)

J-P. Douliez, C. Gaillard, L. Navailles and F. Nallet, Novel Lipid System Forming Hollow Microtubes at High Yields and Concentration, *Langmuir,* 22, 7, 2942-2945, (2006)

S. Poivet, P. Fabre, F. Nallet, K. Schierholz, G. Abraham, E. Papon, Y. Gnanou, R. Ober, O. Guerret and N-E. El-Bounia, Amphiphilic diblock copolymers with adhesive properties: I. Structure and swelling with water, *Eur. Phys. J. E.,* 20, 273-287, (2006)

C. Patrascu, F. Gauffre, F. Nallet, R. Bordes, J. Oberdisse, N. de Lauth-Viguerie and C. Mingotaud, Micelles in Ionic Liquids: Aggregation Behavior of Alkyl Poly(ethyleneglycol)-ethers in 1-Butyl-3-methyl-imidazolium Type Ionic Liquids, *ChemPhysChem,* 7, 99-101, (2006)

J-P. Douliez, J. Barrault, F. Jerome, A. Heredia, L. Navailles and F. Nallet, Glycerol Derivatives of Cutin and Suberin Monomers: Synthesis and Self-Assemblies, Biomacromolecules, 6, 30-34, (2005)

P. Moreau, L. Navailles, J. Giermanska-Kahn, O. Mondain-Monval, F. Nallet and D. Roux, "Dislocation-loop-mediated smectic melting", Europhys. Lett., 73, 1, 49-54, (2006)

J-P. Douliez, L. Navailles and F. Nallet, "Self-Assembly of Fatty Acid - Alkylboladiamine Salts", Langmuir , 22, 2, 622-627, (2006)

Fast internal dynamics in polyelectrolyte gels measured by dynamic light scattering
P. J. Rasmark, Č. Koňák, P. Štěpánek, C. Elvingson
Polymer Bulletin 54, 335, 2005

Štěpánek P., Tuzar Z., Kadlec P., Kříž J.
A dynamic light scattering study of fast relaxations in polymer solutions
Macromolecules, 40, 2165, 2007

Štěpánek P., Tuzar Z., Kadlec P., Kříž J.
Three-dimensional analysis of dynamic light scattering data: application to self-organized polymer solutions
Int. J. Polymer. Anal. Ch., 12, 3, 2007

Surface patterns of block copolymers in thin layers after vapor treatment
P. Černoch, P. Štěpánek, J. Pleštil, M. Šlouf, A. Sidorenko, M. Stamm
European Polymer Journal, 2007, accepted

Černoch P., Krumbholcová E., Martinová L., Přádný M., Štěpánek P., Michálek J. , Synthesis,

electrospinning and QELS characterization of 2-hydroxyethyl methacrylate - 2-ethoxyethyl methacrylate copolymer, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, bstract PC 64, p. 129

Gromadzki D., Makuška R., Lokaj J., Janata M., Netopilík M., Štěpánek P. , Synthesis of ion-containing graft copolymers by photoiniferter radical polymerization, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract PC 36, p. 101

Ryukhtin V., Tuzar Z., Štěpánek P., Pranzas K., Microscopic structure of diblock copolymer solutions in partially miscible solvents studied by USANS, 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006, Abstract PC 37, p. 102

Černoch P., Gromadzki D., Štěpánek P., Structures of block copolymer thin layers, Symposium on Nano Bio Integration, Tokyo 2006

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Czech TV – shootage on nanostructured polymer materials on October 4, 2006

1 D. Patents and industry collaborations

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

Intraproject meetings:

- June 2006 - meeting of the investigators of the project in Saclay (Stepanek, Diat, Nallet)
- July 2006 - meeting of the investigators of the project in Prague (Stepanek, Diat, Nallet)
- October 2006 - meeting of the investigators of the project in Prague (Stepanek, Nallet)
- November 2006 - meeting of the investigators of the project in Bordeaux (Stepanek, Nallet)
- December 2006 - meeting of the investigators of the project in Saclay (Stepanek, Diat)

Networking with other CRP

- SONS workshop in Prague, October 2006, organized by this CRP, see Part 3

1 F. Participation in other conferences

Please list only the most relevant

F. Nallet - XIII International Conference on Small-Angle Scattering, July 9-13 2006, Kyoto, Japan

F. Nallet - Structure and Dynamics in Soft Matter – Beyond Self-Organization and Hierarchical

Structures, July 15-16 2006, Yukawa Institute for Theoretical Physics, Kyoto, Japan

O. Diat - 35eme colloque of GFP ENCPB Paris
"Ionomères séquencés: application pour la pile à combustible. »

O. Diat - Invited seminar Argonne National Laboratory, IPNS « Membrane for fuel cell pictured by neutrons", June 2006

P. Stepanek - 41st World Polymer Congress 'Macro', Rio de Janeiro 2006

P. Stepanek - 45th Microsymposium on Structure and Dynamics of Self-organized Macromolecular Systems, Prague 2006

P. Stepanek - Self-organized Nanostructures (SONS) Conference, Pisa 2006

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

Dr. A. Zinchenko, postdoctoral fellow, 1.11.2004 - 31.1.2005
Mr. D. Gromadzki, PhD student, 1.3.2005 – 30.8.2005
Mr. Jiri Panek, PhD student, 1.4.2006 - 31.8.2006

EUROPEAN SCIENCE FOUNDATION	**EUROCORES Programme** European Collaborative Research **SONS** **Self-Organized NanoStructures**

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number: 02-PE-SONS-126 Acronym / Short Title: MOL-VIC Full Title: One-dimensional molecular self-assembly on vicinal surfaces Project Leader name: Enrique Ortega Project Leader affiliation: Universidad del País Vasco institutional home page (URL): http://www.ehu.es/ project-related home page (URL): http://dipc.ehu.es/ortega/SONS.html Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator: Enrique Ortega, Universidad del País Vasco
Total Funding amount of the IP *(to be corrected by the PI)*
IP 2
Principal Investigator: Richard Berndt, Universität Kiel
Total Funding amount of the IP *(to be corrected by the PI)*
IP 3
Principal Investigator: Enrique Michel, Universidad Autónoma Madrid
Total Funding amount of the IP *(to be corrected by the PI)*
IP 4
Principal Investigator: Karsten Horn, Fritz Haber Institut Berlin
Total Funding amount of the IP *(to be corrected by the PI)*
AP 1
Principal Investigator: André Gourdon, CEMES Toulouse

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The general aim of the CRP is self-assembling one-dimensional (1D) supramolecular structures using vicinal surfaces as primary templates, and characterizing their electronic properties with surface science techniques, such as scanning tunneling microscopy/spectroscopy (STM), core-level and angle-resolved photoemission (XPS, ARPES), and x-ray absorption (NEXAFS) spectroscopies. With this purpose in mind, the MOL-VIC CRP puts together the necessary expertises in synthetic chemistry (AP1), STM characterization (IP1,IP2) and electron spectroscopies (IP1,IP3,IP4). The main achievements can be summarized in the following way:

ACHIEVEMENTS (REFERENCES ARE LISTED IN APPENDIX 1A AND 1B)

1.- Template fabrication, characterization and tuning:
IP1 and IP3 have achieved a successful control and characterization of vicinal surfaces [1,6-9]. A number of noble metal surfaces have been studied, ranging from vicinal Cu(111) and Au(111) to Ag/Cu(111) superlattices. The electronic properties and their relation to the surface structure have been properly determined. The key issue is the way surface electrons scatter at step edges. Strong scattering and electron confinement within terraces is observed at large terraces or within Cu nanostripes in Ag/Cu(111) superlattices, whereas weak scattering and propagation across the steps characterizes narrow terraces and faceted surfaces. Exotic properties of the step scattering, such as the downhill/uphill asymmetry and the bulk absorption have also been studied. Angle-resolved photoemission and synchrotron radiation experiments required a strong collaborative research.

2.- Self-assembled supramolecular structures on flat crystals.
a) IP4 has explored the use of circular dichroism in core level photoemission to determine single molecule chirality with atomic sensitivity [15,20]. Extensive studies of the monotartrate and bitartrate phase on Cu(110) showed detailed intensity patterns, and supported previous conclusions about the use of this methods for studying the chiral nature of adsorbed species.
b) IP1, IP4 and AP1 have collaborated in X-ray absorption (NEXAFS) studies of self-assembled supramolecular monolayer structures [4,5]. Linear aromatic molecules with complementary end-group functionalization, namely NTCDI and BDG, were specifically synthesized by AP1, and studied as single molecule assemblies or as binary mixture networks on Au(111). We found the characteristic fingerprints of atomic species inside the molecules, and specially, the spectroscopic signatures of the hydrogen bond in NEXAFS spectra.
c) IP 4 has investigated self-assembly of a prochiral molecule (dicarboxy-stilbene, DCSB) that acquires a chiral character upon adsorption, into several enantiomericall pure as well as racemic structures of different handedness, using STM, combined with a photoemission study of the specific bonding mechanism of DCSB on Cu (110).

Moreover, the possibility to use molecules which may change their conformation upon irradiation ("molecular switches") was explored in a photoemission and NEXAFS study of stilbene on Cu(111), in order to establish the detection of cis- and trans- conformations in the adsorbed state; parallel gas phase measurements were also carried out.
d) IP3 has investigated the formation of supramolecular structures of pentacene and tetracene on Cu(110) (work unpublished). Combining STM (in collaboration with IP1) and photoemission, a complete picture of the self-assembling process has been obtained. At low coverages one-dimensional structures are formed, which converge into a two-dimensional array of wires at monolayer coverages.

5.- One-dimensional self-assembly of tailored molecules on vicinal surfaces:
Experiments were carried out by IP1, IP2, IP3 and AP1, in collaboration and in parallel, combining STM, photoemission and X-ray absorption experiments [2, unpublished]. In general, collaborative experiments proved that the philosophy of the initial project was correct, i.e., that vicinal surfaces and molecules with appropriate shape and functionalization can be combined to produce a well-oriented array of one-dimensional supramolecular structures.
a) IP2 has investigated self-assembly of C_{60} fullerene nanostructures using low-temperature STM. On Au(433) the preferential adsorption of C_{60} at step edges combined with the facetted surface lead to fullerene nanostripes with high structural perfection [11,12].
b) On Au(788), IP1 has obtained a sharply defined nanomesh (4 nm x 7.2 nm square superlattice) of C_{60} fullerene clusters made of 4 rows of 4-5 molecules [10]. IP2 has observed the same nanomesh for C_{70} fullerenes (work unpublished). Such systems have been explored with X-ray photoemission and absorption spectroscopy by IP1, IP2, and IP3 during joint synchrotron experiments [2]. Despite their structural resemblance, the NEXAFS spectra are remarkably different from the C_{60} or the C_{70} nanomesh. C_{60} spectra are analogous to those of the flat monolayer, with a minor metallization at cluster edges. In contrast, C_{70} spectra exhibit distinct nanomesh features, probably associated to a stronger surface/molecule bonding at step edges [xx].
c) On Au(788), IP1 and AP1 have carried out the STM characterization of tailored one-dimensional supramolecular structures in a mixture of synthetic molecules (NTCDI and BDG) [4]. Using faceted Au(111) with a lateral variation of step lattice constant, a number of different phases have been identified. Among them, a packed structure of one-dimensional binary wires, which line up along the steps.
d) On Au(788), IP2 has performed STS experiments with PTCDA molecules [12,13]. Tunneling spectroscopy on single molecules belonging to different adsorption domains exhibits an energy shift of the lowest and second-to-lowest unoccupied molecular orbital of 0.35 eV, which can be traced back to hydrogen bond-mediated intermolecular interaction.
f) On Au(788), IP2 has shown that cobalt-phthalocyanine forms molecular wires due to a preferential occupation of step edges [14]. Tunnelling spectroscopy in the centre of the molecule reveals cobalt d-orbital related features, while spectroscopy on the benzene rings shows the lowest unoccupied molecular orbital.

NEW DIRECTIONS AND IDEAS
a) The strong dependence of molecular assemblies on the step lattice periodicity, as observed for PTCDA, BDG, and NTCDI on Au(111), suggests a thorough, prospective STM search of distinct structures using curved surfaces. The latter exhibit a somooth variation of the step superlattice constant, and are already being tested by IP1.

b) Our data prove STS as the best spectroscopic tool to determine important spectroscopic information around the Fermi energy in a straightforward way, such as the HOMO-LUMO gap. Thus, STS experiments must be pursued in all molecular structures.
c) The spectroscopic fingerprints of the H-bonding are found to mainly affect higher energy σ-like orbitals, which are better investigated with valence-band photoemission and NEXAFS. In particular, NEXAFS, whose spectra are free of the strong emission from the substrate that shadows the photoemission spectra. Nonetheless, the weakness of H-bonding signatures in NEXAFS suggests more complex experiments using light polarization and well-defined geometries.
d) Our CRP has prompted the collaboration with theory groups (Arnau, Lorente) that is going to be strengthened in the future.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

The most attractive systems have been investigated only with STM. The electron spectroscopy characterization (by NEXAFS and photoemission) has not been carried out yet. Among them, all the linear structures that self-assemble on v-Au(111): the striped fullerene and PTCDA structures on v-Au(111), and the NTCDI/BDG, CoPc and PTCDA molecular wires that decorate steps on v-Au(111). Such fine systems are difficult to achieve during short synchrotron beam times, and hence require a sustained effort in time and people. This was not possible during the short duration of the CRP.

STS experiments are required to accurately determine the electronic states around the Fermi energy in a number of molecular structures, such as the NTCDI/BDG binary chains. The STS experiments could only be performed by IP2, and many molecular structures are yet to be analyzed.

A number of diffrent molecule/surface systems have been also tested, either on flat or vicinal surfaces, but these studies are far of being completed. These comprise acid C_{70} fullerenes (called PCBA) on Au(788) and vicinal Ag(111), BDG and NTCDI networks on Cu(111).

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

The combined, surface-sensitive technique approach to molecular self-assembly provides the more direct and fresh view of basic structural and electronic properties in self-asembled, supramolecular systems. For instance, single molecule scanning tunneling spectroscopy has shown a considerable

strength to determine surface/molecule interactions. NEXAFS, and in general electron spectroscopic techniques are still to be fully exploited in the characterization of fine molecular systems. All in all, we belive that the surface approach must be supported with new exotic ideas, such as in-situ induced supramolecular bonding, molecular chain polimerization, etc.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

The flexibility compared to regular european frame program projects.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

For a complex, multidisciplinary project more time is required. The three year frame appears too short to be 100% successful

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

1. "Tuning surface state dimensionality in Cu nanostripes", J. Lobo, E. G. Michel, A. Bachmann, S. Speller, J. Kuntze, and J. E. Ortega, Phys. Rev. Lett. **93**, 137602 (2004).

2. "Electronic structure of C_{60} on Au(887)", F. Schiller, M. Ruiz-Osés, J. E. Ortega, P. Segovia, J. Martínez-Blanco, B. P. Doyle, V. Pérez-Dieste, J. Lobo, N. Néel, R. Berndt, y J. Kröger, J. Chem. Phys. **125**, 144719 (2006).

3. "Self-assembly of heterogeneous supramolecular structures with uniaxial anisotropy", M. Ruiz-Osés, N. González-Lakunza, I. Silanes, A. Gourdon, A. Arnau, J. E. Ortega, J. Phys. Chem. B **110**, 25573 (2006).

4. "Spectroscopic fingerprints of amine and imide functional groups in supramolecular monolayers", M. Ruiz-Osés, N. González-Lakunza, I. Silanes, A. Gourdon, A. Arnau, J. E. Ortega, Chem. Phys. Chem. (in press).

5. "Identifying functional end-group features in self-assembled π-conjugated supramolecular monolayers", M. Ruiz-Osés, T. Kampen, N. González, I. Silanes, A. Arnau, A. Gourdon, K. Horn, Annual report BESSY p. 308 (2007).

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

6. "Scattering of surface states at step edges in nanostripe arrays", F. Schiller, J. Cordón, M. Ruiz-Osés, and J. E. Ortega, Phys. Rev. Lett **95**, 066805 (2005).

7. " "One-dimensional versus two-dimensional electronic states in vicinal surfaces", J. E. Ortega , M. Ruiz-Osés, J. Cordón, A. Mugarza, J.Kuntze, and F. Schiller, New Journal of Phys. **7**, 101 (2005).

8. "Finite size effects in surface states of stepped Cu nanostripes", J. E. Ortega, M. Ruiz-Osés, and J. Kuntze, Phys. Rev. B **72**, 195416 (2005).

9. "Modeling nanostructures with vicinal surfaces", A. Mugarza, F. Schiller, J. Kuntze, J. Cordón, M. Ruiz-Osés, and J. E. Ortega , J. of Phys. C **18**, S27 (2006).

10. "Highly Periodic Fullerene Nanomesh" N. Néel, J. Kröger, and R. Berndt, *Adv. Mat.* **18**, 174 (2006)

11. "Fullerene Nanowires on a Vicinal Gold Surface" N. Néel, J. Kröger, and R. Berndt, *Appl. Phys. Lett.* **88**, 163101 (2006)

12. "Molecules on vicinal Au surfaces studied by scanning tunnelling microscopy" J. Kröger, N. Néel, H. Jensen, R. Berndt, R. Rurali, and N. Lorente, *J. Phys.: Condens. Matter* **18** S51–S66 (2006)

13. "Molecular orbital shift of perylenetetracarboxylic-dianhydride on gold" J. Kröger, H. Jensen, R. Berndt, R. Rurali and N. Lorente, *Chem. Phys. Lett.* **438** 249 (2007)

14. "Self-organization of cobalt-phthalocyanine on a vicinal gold surface revealed by scanning tunnelling microscopy" (in press) J. Kröger, H. Jensen, N. Néel, and R. Berndt, *Surf. Sci.* (2007), doi:10.1016/j.susc.2007.04.091

15. "Circular Dichroism in Photoelectrons from Adsorbed Chiral Molecules", J. W. Kim, J. H. Dil, Th. Kampen, and K. Horn, Proceedings of SRI 2006, in press.

16. "Conformaional Isomers of Stilbene on Si(100)", Ph.Schmidt, T.U.Kampen, J.H.Dil, and K.Horn Surface Science, (in press).

17. "Electronic structure of biphenyl on Si(100)", M. Cranney, G. Comtet, G. Dujardin,, J.W. Kim, T. Kampen, K. Horn, M. Mamatkulov, L. Stauffer and Ph. Sonnet, Surface Science, (in press).

18. "Thermal decomposition of ehtylene on Si(111): formation of the Si(111) √3 x √3 carbon structure", J.W.Kim, T.U.Kampen, K.Horn, M.-C.Jung, , Surface Science **601** 694–698 (2007).

19. "Quasicrystalline electronic states of a one-dimensionally modulated Ag film", P. Moras, W. Theis, L. Ferrari, S. Gardonio, J. Fujii, K. Horn, and C. Carbone, , Phys.Rev.Lett. **96**,156401 (2006).

20. "Atom-specific identification of adsorbed chiral molecules by photoemission", J. W. Kim, M. Carbone, J. H. Dil, M. Tallarida, R. Flammini, M. P. Casaletto, K. Horn, and M. N. Piancastelli, Phys.Rev.Lett. **95**, 107601 (2005).

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

1. BESSY Highlight "On or Off - Identifying isomerization in molecular switches" Bessy Annual Report 2006.

2. BESSY Users' Meeting, December 2006 - Poster prize for "Identifying isomerization in molecular switches"

1 D. Patents and industry collaborations

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

1 F. Participation in other conferences

Please list only the most relevant

1. "Supramolecular self-assembly on flat and vicinal Au(111)", M. Ruiz-Osés, F. Schiller, J. E. Ortega, A. Gourdon, N. González, I. Silanes, A. Arnau, ECOSS-24, Paris (France), Septembre 2006. *Poster.*
2. "Self-Assembly of Heterogeneous Supramolecular Structures with Uniaxial Anisotropy", M. Ruiz-Oses, N. Gonzalez-Lakunza, I. Silanes, A. Gourdon,☐ A. Arnau, and J. E. Ortega, , Symposium on Surface Science 2007, 3S'07, March 2007, Les Arcs (France).*Poster..*
3. "Self-Assembly of Heterogeneous Supramolecular Structures with Uniaxial Anisotropy", M. Ruiz-Oses, N. Gonzalez-Lakunza, I. Silanes, A. Gourdon,☐A. Arnau, and J. E. Ortega, E-MRS 2007 Spring Meeting, Mayo 2007, Strasbourg (France). *Poster*
4. "Self-assembly of binary supramolecular networks on Au(111): geometry and electronic states", M. Ruiz-Osés, N. González-Lakunza, I. Silanes, A. Gourdon,☐ A. Arnau, Th. Kampen, K. Horn, and J. E. Ortega, 15th International Conference on Vacuum Ultraviolet Radiation Physics, VUV XV, July 2007 Berlin, (Germany). *Oral*
5. "Adsorption of planar aromatic hydrocarbons on Cu(110) and Ag(110): self assembling and electronic structure" J. Martínez-Blanco, V. Joco, L. Walczak, D. Sayago, M. Ruiz-Oses, I. Voborkik, P. Segovia and E.G. Michel 24th European Conference in Surface Science (ECOSS-24), September 2005, Paris (France) *Oral*
6. "Tartaric Acid adsorbed on Cu(110): Circular Dichroism and Structure", Kampen T. U., Dil J. H.,Kim J. W., Schmidt P. M., Horn K., Parschau, M. and Ernst K.-H., 10th International Conference on the Formation of Semiconductor Interfaces (ICFSI-10) 2005 (Aix-en-Provence), *Poster*
7. "Conformation of Adsorbed Molecules: Stilbene on Si(100)", Schmidt P. M., Kampen T. U., Dil J. H. and Horn K., 1st EuCheMS Chemistry Congress 2006 (Budapest), *Poster*
8. "Optical anisotropy in a self-assembled molecular film", Kampen T. U., Silaghi S., Schmidt P. M., Cortes R., Mascaraque A., Esser N. and Horn K., DPG Spring Meeting 2007 (Regensburg), *Poster*
9. "Identifying isomeric switching – Stilbene on Si(100) and Cu(110) surfaces", Schmidt P. M., Kampen T. U. and Horn, K., DPG Spring Meeting 2007 (Regensburg), *Poster.*
10. "Tartaric acid adsorbed on cu(110): circular dichroism and structure", Ph. Schmidt, T.U. Kampen, J.H. Dil, and K. Horn, 10th International Conference on the Formation of Semiconductor Interfaces (ICFSI-10) 2005 (Aix-en-Provence).
11. Conformation of adsorbed molecules: Stilbene on Si(100), Schmidt P. M., Kampen T. U. and Horn K., DPG-Spring Meeting 2006 (Dresden). *Oral*
12. "Identifying isomerization–combined experimental and theoretical NEXAFS studies", Schmidt P. M., Horn K. and Kampen T. U. Kolczewski C. and Hermann K. & Püttner R., DPG-Spring Meeting 2007 (Regensburg). *Oral*

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

1.- Néel, Nicolas, Postdoctoral position 01/05/2004 to 15/04/2006

2.- Kampen, Thorsten, Postdoctoral position

3.- Ruiz-Osés, Miguel, Ph. D. student 01/06/2004 to 31/07/2005 (thesis to be completed).

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number: 02-PE-SONS-130 Acronym / Short Title: NETSOMA Full Title: Nanoscale Electrical Transport in Self-Organized Molecular Assemblies Project Leader name: Prof. Henning Sirringhaus Project Leader affiliation: University of Cambridge Institutional home page (URL): http://www.cam.ac.uk Project-related home page (URL): http://www-oe.phy.cam.ac.uk Reporting period: from 1 January 2006
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator (name & affiliation): Prof. Rene Janssen & Prof. Bert Meijer, Technical University of Eindhoven, The Netherlands
Total Funding amount of the IP: €346500
IP 2
Principal Investigator (name & affiliation): Prof. Paul Smith, ETH Zuerich, Switzerland
Total Funding amount of the IP: CHF 174493
IP 3
Principal Investigator (name & affiliation): Dr. Martin Nielsen, Riso National

Laboratory, Denmark
Total Funding amount of the IP*:* €222000
IP 4
Principal Investigator (name & affiliation): Prof. Henning Sirringhaus & Prof. Sir Richard Friend, University of Cambridge, UK
Total Funding amount of the IP: €509325
AP 1
Principal Investigator (name & affiliation):

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including

- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The project was focussed on exploring new electronic and optical phenomena arising in well-defined nanoscopic self-assemblies of bi-functional conjugated block copolymers. It brought together four internationally leading groups with complementary expertise in conjugated polymer synthesis (Technical University of Eindhoven), polymer processing (ETH Zuerich), structural characterization of polymers (Riso National Laboratory) and conjugated polymer materials and device physics (University of Cambridge). The project was designed to be highly interdisciplinary and collaborative. Its aim was to design, prepare, process, and characterize electrically, optically and structurally novel conjugated block copolymers, and incorporate them into electronic devices, such as organic field-effect transistors (FETs).

We decided to focus the project on a new class of semiconducting – dielectric diblock copolymers comprising a semicrystalline conjugated polymer semiconductor - regioregular poly-3-hexylthiophene (P3HT) - and a semicrystalline polymer dielectric – polyethylene (PE). This system was selected because of the broad range of processing pathways which are opened up by the ability to control the crystallization of each of the two blocks. Through judicious choice of processing conditions a high level of control over the morphology and microstructure, and the electronic and optical properties in thin solid films can be achieved.

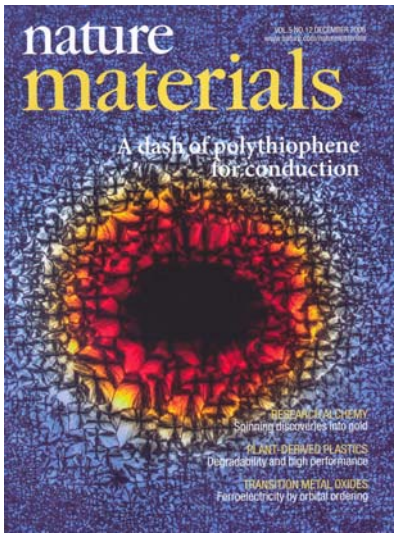
The first key achievement of the project was the synthesis of the diblock-copolymers. The synthesis of functional diblock copolymers is challenging, and a number of different chemical routes were explored. The most successful approach was to synthesize the block copolymer through the chain transfer of olefin-terminated P3HT in the presence of cyclooctene via ring-opening metathesis polymerization (ROMP). Subsequent hydrogenation of the poly(cyclooctene) block yielded high molecular weight, *crystalline-crystalline* P3HT-PE block copolymers (Radano et al., *J. Am. Chem. Soc.,* **127**, 12502, 2005). Polymers of different block lengths were synthesized and these materials formed the basis for the processing, structural and device investigations. More recently we have also extended this approach to other block copolymers comprising, for example, polyfluorene or perylene diimides and PE.

The second breakthrough of the project was the development of processing pathways which allowed controlling the microstructure and microscale phase separation of these block copolymers. For this purpose it was essential to study the thermodynamic phase behaviour as a function of solvent, concentration, relative length of the two blocks and temperature. Guided by the insight gained from these phase diagrams we discovered that is was possible to select processing conditions such that either the polyethylene block or the polythiophene block could be crystallized first while the other block remained molten.

The next important step was a careful structural analysis of the film microstructure and phase separation by X-ray diffraction and electron microscopy. It was found that if the P3HT was allowed to crystallize in an environment of molten PE a much higher degree of crystallinity could be obtained than for process conditions in which the PE crystallized first. We also achieved a detailed understanding of the thermodynamical processes that govern the formation of the microscale phase separation in the liquid phase.

Another key breakthrough of the project was the demonstration of superb electrical properties when integrating these highly crystalline P3HT-PE blockcopolymer films into

organic FET devices. We were able to show that even for very small concentration of P3HT high-field effect mobilities up to 0.05 cm^2/Vs could be achieved. This is comparable with state-of-the-art FETs based on P3HT homopolymers, but the block copolymers exhibit much better mechanical properties. The diblock copolymer films could be stretched to an elongation to break of more than 660 % while P3HT homopolymers are much more brittle and already break at 13% elongation (Mueller, Adv. Funct. Mat., in press).



Going beyond the scope of the original proposal we realized that the physical mechanisms which result in such excellent performance should not only apply to block copolymers but also to blends of the two components. We showed that in both the blends as well as the block copolymer due to a highly favourable, crystallization-induced phase segregation of the two components, during which the semiconductor is predominantly expelled to the surfaces of cast films, vertically stratified structures can be obtained in a one-step process. Incorporating these as active layers in polymer field-effect transistors (FETs), we showed that the concentration of the semiconductor can be reduced to values as low as 3 wt% without any degradation in device performance with mobilities reaching values up to 10^{-1} cm^2/Vs. This is in stark contrast to blends comprising an amorphous insulating polymer, for which significant reduction in electrical performance upon blending was reported. This work was published in Nature Materials and was highlighted on the cover of the issue (Goffri, Nature Materials 5, 950 (2006).

Blends and blockcopolymers behave in many respects similarly, but there are also key differences. The block copolymers exhibit much improved mechanical properties, and there are also a number of key difference in the temperature dependence of phase separation and the microscopic polymer chain morphology that have recently been investigated in significant detail on the basis of structural, electrical and optical characterisation (Goffri et al., in preparation).

The interdisciplinary and collaborative approach of the project (evident also from the number of joint publications) was the key to the success of this project. We feel strongly that the breakthrough results detailed above could not have been obtained by any of the individual groups alone, but were enabled by a close cooperation between polymer chemistry, polymer processing, structural characterization and device physics. It would not have been possible to find the necessary skills for this project in a single country, and the SONS scheme enabled this collaboration.

A number of new research directions have emerged from the project. We believe that crystalline-crystalline block copolymers provide a new approach to high-performance multi-functional materials that allow a high level of control over microstructure and properties through processing. Crystalline-crystalline multi-component systems offer expanded flexibility for realizing high-performance semiconducting architectures at drastically reduced materials cost with improved mechanical properties and environmental stability without the need to design all performance requirements into the active semiconducting polymer itself. We expect that this approach can be applied in a number of different research and application fields, such as organic solar cells, or functional, truly flexible plastic substrates and films for sensing applications. Much of the physics of functional crystalline-crystalline block copolymers and blends still remains to be understood, and we are already aware of research activities in a number of leading polymer physics groups which have been stimulated by our results. In terms of industrial impact the project has resulted in one joint patent application covering the use of functional crystalline-crystalline multicomponent blockcopolymers and blends in electronic devices. Negotiations with two leading companies in the field of organic electronics are currently underway for licensing this IP.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

The original project proposal had a somewhat broader materials scope and we had planned to investigate not only semiconductor-dielectric, but also semiconductor-semiconductor block copolymers. During the first year of the project we attempted to synthesize a number of different systems, but the synthesis of semiconductor-semiconductor block copolymers turned out to be very challenging, and appeared to be limited to relatively small molecular weight material that did not show promise for exploring polymer processing – property relationships. When we discovered the successful ROMP approach to P3HT-PE block copolymers that produced high-quality, high molecular weight block copolymers in good yield we decided to focus on this system as a model system for crystalline-crystalline functional block copolymers. In retrospect this decision was right since the level of focus we were able to apply to the PE-P3HT system allowed us to make significant advances on the processing, physical understanding and device performance (for details see above). We are now in a position to apply the understanding and insight gained with the PE-P3HT model system to other functional systems, and this could form the basis of a follow-on project.

In all other respects the project proceeded as planned, and, in particular, resulted in the high level of collaborative research activities that had been intended.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

At present there is no new research project which has directly followed on from the project. However, we are very keen to continue the collaboration which was initiated by the project. We have so far decided against submitting an FP7 project due to the high level of administrative overhead involved and the difficulty of constructing a focussed scientific project while still ticking all the boxes required for a successful FP7 project. We are actively looking for suitable funding opportunities that would allow us to continue and expand the research directions and collaborations initiated by the SONS project. A natural next step will be to apply the knowledge gained with crystalline-crystalline semiconductor – dielectric systems and extend this to other functional systems, such as semiconductor-semiconductor block copolymer for applications such as organic photovoltaics.

As discussed above there has been significant industrial interest in the project results and negotiations with two leading companies are ongoing to licence the IP generated in the project. It is possible that over the next 2-3 years the high-performance multicomponent materials and processing techniques developed in the present project will enable significant technological advances, for example, enable device applications where a high level of mechanical flexibility is required of the device which is currently not achievable with simple single-component systems. Also we observed that the environmental stability of the block copolymer and blend systems is superior to that of the single-component semiconducting polymer. Environmental stability is one of the most important performance metrics for selecting materials for electronic device applications. Currently, there is a high level of interest in the industrial community on multicomponent active layers, and our research results have contributed to, and stimulated this development.

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

We consider the field of functional block copolymers and other multicomponent systems a very attractive research direction for future research priorities of ESF since it brings together the traditional fields of polymer science and organic electronics. Progress in this area can only be made if the knowledge of conventional polymer science (processing, polymer

physics) is applied to novel functional systems with desired electrical, optical, sensing and other properties. This is because of the need to control to a high level the microstructure and morphology of the polymers in order to achieve specific functions and device performance. Such a highly interdisciplinary and collaborative field is ideally suited for science-focussed collaborative projects enabled by funding from ESF.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

Often highly interdisciplinary research projects like NETSOMA cannot find all necessary levels of expertise within a single country, and require international research collaborations. Unfortunately, often such international collaborations involve a significant level of administrative overhead, particularly if funded under the European Framework program. This is not always appropriate, in particular for relatively small basic science projects like NETSOMA where fastest progress can be made if the consortium can focus on the scientific interaction. For such projects a high level of autonomy is beneficial to enable the participants to follow the most exciting directions of research that depend on the outcome of experiments. It is our experience that a highly collaborative scientific project should not be too narrowly constrained by a predefined work plan and list of deliverables. We feel strongly that the EUROCORES program has provided such a framework that fosters dynamic scientific collaborations and has allowed us to continuously engage in the most exciting lines of research.

Most of the key interactions in the NETSOMA project have happened within the CRP, but we have also benefited from the networking with other projects under the same EUROCORES scheme, and the thematic workshops that were organised.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

In our opinion the EUROCORES scheme has been a highly successful instrument. The initial project selection and approval process was lengthy and complex due to the coordination needed between the different national funding agencies, and maybe there are ways to streamline the project selection and negotiation process. However, in our opinion the EUROCORES funding scheme with its focus on highly collaborative, science-focussed projects fills a gap in the international funding landscape that is not met by other instruments such as the European framework projects and should be continued.
The EUROSCORES SONS program provided an ideal platform for expanding our existing cross-disciplinary co-operations, which was of extraordinary benefit not only for the proposed project, but the European research area in general. In addition, one should not forget invaluable educational benefits. The intrinsic, high multi-disciplinary and international character of the proposed research provided excellent interdisciplinary training opportunities for the master-/ Ph.D.-students and the postdoctoral fellows involved in the research, and offered them the great possibility to work with the groups of some of the key scientists in the respective fields. Therefore, we can only conclude that Network Programs such as EUROSCORES SONS provided highly beneficial opportunities for research groups and science in Europe.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

- NA

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

- Multicomponent semiconducting polymer systems with low crystallization-induced percolation threshold
  Goffri S, Muller C, Stingelin-Stutzmann N, Breiby DW, Radano CP, Andreasen JW, Thompson R, Janssen RAJ, Nielsen MM, Smith P, Sirringhaus H
  Nature Materials 5, 950-956 (2006)

- Crystalline-crystalline block copolymers of regioregular poly(3-hexylthiophene) and polyethylene by ring-opening metathesis polymerization
  Radano CP, Scherman OA, Stingelin-Stutzmann N, Smith P, Janssen RAJ
  Journal of the American Chemical Society, 127, 12502-12503 (2005)

- Tough, Semiconducting Polyethylene-Poly(3-hexylthiophene) Diblock-Copolymers
  Muller C, Goffri S, Andreasen JW, Breiby DW, Chanzy HD, Janssen RAJ, Nielsen MM, Radano CP, Sirringhaus H, Smith P, Stingelin-Stutzmann N
  Advanced Functional Materials, in press

- Molecular-weight dependence of interchain polaron delocalization and exciton bandwidth in high-mobility conjugated polymers
  Chang JF, Clark J, Zhao N, Sirringhaus H, Breiby DW, Andreasen JW, Nielsen MM, Giles M, Heeney M, McCulloch I
  Phys. Rev. B 74, 115318 (2006)

- Comparison of the chain length dependence of the singlet and triplet excited states of oligofluorenes,
  Wasserberg D, Dudek SP, Meskers SCJ, Janssen RAJ
  Chemical Physics Letters, 411, 273-277 (2005)

- Synthesis and Energy-Transfer Properties of Hydrogen-Bonded Oligofluorenes.
  Dudek SP, Pouderoijen M., Abbel R, Schenning APHJ, Meijer EW
  Journal of the American Chemical Society. 127, 11763-11768 (2005)

- Alternating donor-acceptor block copolymers
  Radano CP, Janssen RAJ, Meijer EW
  Pol. Mater. Sci. Eng. (ACS Div.) 91, 740-741 (2004)

- Synthesis and characterization of poly(3-hexylthiophene)-polyethylene block copolymers
  Nielsen CB, Janssen RAJ
  Pol. Mater. Sci. Eng. (ACS Div.) 96, 576-577 (2007).

Papers in preparation:

- Comparison between crystalline-crystalline polymer semiconductor – polymer dielectric blends and blockcopolymers
  Goffri S, Muller C, Andreasen JW, Breiby DW, Janssen RAJ, Nielsen MM, Radano CP,

Sirringhaus H, Smith P, Stingelin-Stutzmann N
In preparation

- Microstructure of crystalline-crystalline polymer semiconductor – polymer dielectric blends and blockcopolymers
Breiby DW, Andreasen JW, Nielsen MM, Goffri S, Muller C, Janssen RAJ, Radano CP, Sirringhaus H, Smith P, Stingelin-Stutzmann N
In preparation

- Phase behaviour of crystalline-crystalline polymer semiconductor – polymer dielectric blends and blockcopolymers
Muller C, Goffri S, Andreasen JW, Breiby DW, Janssen RAJ, Nielsen MM, Radano CP, Sirringhaus H, Smith P, Stingelin-Stutzmann N
In preparation

- Crystalline-crystalline diblock copolymers of polythiophene and polyethylene: Synthesis and characterization
Nielsen CB, Fonrodona M, Veldman D, Janssen RAJ, Goffri S, Sirringhaus H, Muller C, Stingelin-Stutzmann N, Smith P,
In preparation

- Copolymers of polyethylene and perylene diiimide through ring-opening metathesis polymerization.
Nielsen CB, Fonrodona M, Veldman D, Janssen RAJ,
In preparation

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

1 D. Patents and industry collaborations

- Patent application UK
High-performance organic field-effect transistors based on dilute, crystalline-crystalline polymer blends and block copolymers
Goffri S, Muller C, Stingelin-Stutzmann N, Radano CP, Janssen RAJ, Smith P, Sirringhaus H
312321.GB/PRS/PSR

- Industrial collaborations with Merck (supply of P3HT polymers, evaluation of TFT performance and reliability based on materials developed here) and Plastic Logic Ltd (device evaluation).

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

We held regular 6 monthly project meetings rotating the location of the meeting between the different partner institutions. These meetings were held to report on project results, to discuss scientific results and project direction, to define interactions between partners and plan collaborative experiments. A very intense, effective and fruitful collaboration was set up in this way.
Graduate students and post-doctoral researchers from one partner have visited other partners for training and joint experiments at regular intervals, typically for periods of 1-2 weeks. The following list provides some examples: Dr. Chris Radano visited ETH for several weeks to help developing processing methodologies for the polymers which he synthesized at TUE. A two-day workshop on processing of poly(3-hexylthiophene) and friction-transferred PTFE layer fabrication took place at ETH Zurich at February 10/11, 2005 to produce films for the X-ray characterization at Risø. Christian Muller, the PhD student at ETH, came to Cambridge for several visits to help integrating processing methods into the device fabrication processes. Shalom Goffri, the PhD student from Cambridge, went to ETH on a number of occasions to learn the processing methods. From September 29 – October 2, 2006 the team performed joint synchrotron Small-Angle X-ray characterisation of thin-film structures produced at ESRF Grenoble, France.

1 F. Participation in other conferences

Please list only the most relevant

Oral presentations:

- Invited presentation (S. Goffri) – American Chemical Society Annual Meeting 2007, Chicago, USA (2007)
- Invited presentation (H. Sirringhaus), Organic Microelectronics Workshop IEEE-MRS-ACS, Toronto, Canada (2006)
- Invited presentation (H. Sirringhaus) – Polymer Physics Gordon conference, New London, USA (2006)
- Invited presentation (H. Sirringhaus) – Materials Research Society Fall Meeting 2006, Boston, USA (2006)
- Invited presentation (N. Stingelin-Stutzmann) , July 30 - August 4, 2006
  Gordon Conference on Electronic Processes in Organic Materials, Mount Holyoke College, South Hadley, MA, USA
  Organic electronics from vitreous, solution-processed rubrene hypereutectics
- Invited presentation (N. Stingelin-Stutzmann) 13-17 August, 2006
  SPIE Conference on Optics & Photonics, San Diego, California, USA
  Organic electronics from vitreous, solution-processed rubrene hypereutectics
- Dr. N. Stingelin-Stutzmann, June 29 - July 1, 2006
  SONS Conference, Pisa, Italy
  Structure-property relationship of crystalline conjugated block-copolymers
- C. Müller, S. Goffri, Dr. N. Stingelin-Stutzmann, Dr. D.W. Breiby, July 1, 2006
  SONS Confrence, Pisa, Italy
  P3HT-PE block copolymers and blends - processing, microstructure and electronic properties
- C. Müller, August 14, 2006
  SPIE Conference on Optics & Photonics, San Diego, California, USA
  Tough semiconducting copolymers and polymer blends - A route towards truly flexible plastic electronics

- C. Müller, August 31, 2006
  1st European Chemical Congress (EuroChems), Budapest, Hungary
  Tough semiconducting PE-P3HT diblock copolymers - A route towards truly flexible plastic electronics

Poster presentations

- C. Müller, October 13, 2006
  Swiss Chemical Society Fall Meeting (SCS), Zürich, Switzerland
  Tough semiconducting PE-P3HT diblock copolymers - A route towards truly flexible plastic electronics
- Poster presentation (C. Nielsen) - American Chemical Society Annual Meeting 2007, Chicago, USA (2007)
- Poster presentation (C. Radano) - American Chemical Society Annual Meeting 2004, Philadelphia, USA (2007)

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

PhD students:

- Christian Mueller: Since 1.5.2005 (working together with Dr. Natalie Stingelin-Stutzmann (20%) on the present project, PHD to be completed 2008)
- Shalom Goffri: October 2004-May 2007 (PhD completed)

Post-doctoral research fellows:

- Dr. Christopher Radano: October 2003 – November 2005
- Dr. Stephen Dudek: October 2003 –December 2004
- Dr. Dag Breiby: October 2004 – January 2007
- Dr. Jens Andreasen: October 2004 – January 2007
- Dr. Marta Tello: Jan 2005 – May 2007

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"CRP Name"

Submission deadline:
11 May 2007

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number: 02-PE-SONS-136 Acronym / Short Title: **SALSDON** Full Title: **Self-Assembled Low-Dimensional Semiconductor Nanostructures** Project Leader name: Prof. Eli Kapon Project Leader affiliation: Ecole Polytechnique Fédérale de Lausanne (EPFL) Institutional home page (URL): http://www.epfl.ch/ Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator (name & affiliation): Prof E Kapon, Ecole Polytechnique Fédérale de Lausanne (EPFL) Lausanne, Switzerland Total Funding amount of the IP: **CHF 403,346**
IP 2
Principal Investigator (name & affiliation): Prof D D Vvedensky, The Blackett Laboratory, Imperial College, London SW7 2AZ, United Kingdom Total Funding amount of the IP: **€ 214,796**

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

The main efforts in this project have concentrated on understanding the self-ordering mechanisms of quantum wires (QWRs) and quantum dots (QDs) grown by metalorganic vapour-phase epitaxy (MOVPE) on nonplanar substrates, particularly implemented in the InGaAlAs/GaAs semiconductor compound system. Several unique features of these nanostructures have been demonstrated, including site control, emission wavelength control, and very high uniformity and reproducibility. The collaborative work consisted of fabrication of patterned substrates, regrowth and characterization of the nanostructures using optical spectroscopy methods, and theoretical modelling and simulations.

Since the characteristics of nanostructure and disorder of site-controlled QWRs grown in V-groove are intimately related to the evolution of the surfaces formed on the patterned substrate, we studied in detail this evolution using atomic force microscopy (AFM). After having explained the phenomenon of step ordering on the V-groove patterns, we turned our attention to the phenomena of ordered step bunching on miss-oriented substrates. The formation of ordered step bunches on the patterned substrates was evidenced and characterized in detail.

In another part of the work, we studied the mechanisms of formation of pyramidal QDs on patterned (111)B GaAs substrates. Using a simple model, we showed the importance of precursor diffusion and decomposition on in determining the local growth rates, and hence the QD thicknesses and emission wavelengths. Using this approach, we were able to demonstrate QDs with controlled emission wavelengths, grown side by side on the same substrate. In addition, ordered pyramidal QD arrays with record values of homogeneity across the wafer were made and studied. Inhomogeneous broadening as small as ~4meV was demonstrated, and this while maintaining a large lateral confinement energy.

The central issues for modelling the formation of nanostructures on patterned substrates grown by MOVPE are (i) the presence of highly mobile polyatomic precursors, and (ii) the resulting long characteristic length scales of the surface morphology, which extends to microns. In contrast, during growth by molecular beam epitaxy (MBE), only the atomic constituents of the growing material are deposited onto the surface, which have a far lower degree of mobility, so the pertinent length scales are measured in

nanometers. Thus, for MBE, direct simulation based on the kinetic Monte Carlo (KMC) method is perfectly feasible and has been used to great effect over many years. For MOVPE on patterned substrates, however, KMC simulations at micron length scales are impractical, so continuum descriptions have been used instead to address the basic growth issues. It is in this arena that our modelling efforts have been concentrated. The key theoretical advances are:

Morphological evolution on vicinal patterned substrate

- The development of a model for the motion of (001) ridges on V-grooved GaAs surfaces.
- An understanding of monatomic step ordering mechanisms on patterned nonplanar substrates.
- The determination of the atomistic mechanisms behind the experimentally-observed correlation between interface morphology and luminescence/ transport properties of quantum well heterostructures grown by MOVPE on misoriented substrates.

Continuum Equations for Heteroepitaxial Systems

- The derivation of an evolution equation for strained heteroepitaxial systems.
- Validation of our methodology against KMC simulations.

These modelling schemes were used to explain the ordered step-bunching observed on the V-grooved substrates. Preliminary work has been done for understanding the self-ordering of the pyramidal QDs due to growth rate anisotropy and nano-capillarity.

The combined approach of experimental and theoretical modelling employed in this project allowed to achieve understanding of the self-ordering mechanisms of semiconductor nanostructures that would be difficult to obtain otherwise. The nanostructures developed represent the state of the art of low-dimensional semiconductor structures in terms of uniformity, structural control and optical quality.

4. What did you not achieve in the CRP and why? (max 1 p.)
Please use the original proposal as reference and explain any deviations from the work plan

The only significant change to the project plan was the role played by a code that was developed in earlier work [*Phys. Rev. B* **67**, 075316 (2003)]. In collaboration with Russ Caflisch and his colleagues at UCLA, we developed a method for computing the effect of strain relaxation on the kinetics of heteroepitaxial systems. The calculations that demonstrated the feasibility of that calculation were based on one-dimensional (1D) step trains. We have applied these calculations to 1D profiles on patterned substrates, but the application of this methodology to quantum dots and quantum wires requires full three-dimensional calculations, which represents a significant increase in computational resources. Accordingly, our main effort has been to the development of the code to do this. Caflisch has developed an algebraic multigrid method for this strain problem, which greatly accelerates the

computations and expands its range of applicability, and has been tested on idealized systems of 3D quantum dots.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

The realization of inorganic nanostructures, particularly in semiconductors, is of key importance for future developments in electronics, photonics, and the interface between biological and artificial systems. New programs supporting this direction are necessary for synergy among research groups active in this field in Europe.

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

The added value of being part of a EUROCORES Programme is undoubtedly the collaborative aspect of the projects, especially between multinational theory and experimental groups. Such programmes are difficult, if not impossible, to fund through individual national grant agencies, so the umbrella structure of ESF is paramount.

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

The current program had too few projects on inorganic nanostructures, which prevented reaching a critical mass of activity in this area on the program level. Better balance between work on inorganic and organic nanostructures should be sought in the future.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

A. Dalla Volta, D. D. Vvedensky, N. Gogneau, E. Pelucchi, A. Rudra, B. Dwir, E. Kapon, and C. Ratsch, "Evolution of vicinal ridges on V-Grooved GaAs surfaces", *Applied Physics Letters* **88**, 203104 (2006).

A. L.-S. Chua, N. Gogneau, E. Pelucchi, A. Rudra, B. Dwir, E. Kapon, D. D. Vvedensky, and A. Zangwill, "Morphological evolution of misoriented GaAs(001) surfaces during metalorganic vapor-phase epitaxy", to be submitted to *Applied Physics Letters* (manuscript available upon request).

G. Schusteritsch, N. Gogneau, E. Pelucchi, A. Rudra, B. Dwir, E. Kapon, and D. D. Vvedensky, "Self-limiting growth of quantum nanostructures on patterned surfaces", in preparation.

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

EPFL:

A. Rudra, E. Pelucchi, D.Y. Oberli, N. Moret, B. Dwir and E. Kapon, "Properties of GaAs/AlGaAs Quantum Wells Grown by OMVPE using Vicinal GaAs Substrates", J. Crystal Growth **272**, 615-620 (2004).

T. Otterburg, D. Y. Oberli, M.-A. Dupertuis, N.Moret, E. Pelucchi, B. Dwir, E. Kapon, "Enhancement of the Binding Energy of Charged Excitons in Disordered Quantum Wires", Phys. Rev. B **71**, No. 033301 (2005).

N. Moret, D.Y. Oberli, E. Pelucchi, N. Gogneau, A. Rudra and E. Kapon, "Correlation between optical properties and interfaces morphology of GaAs/AlGaAs quantum wells", Appl. Phys. Lett. **88**, 141917 (2006).

Q. Zhu, E. Pelucchi, S. Dalessi, K. Leifer, M.A. Dupertuis and E, Kapon, "Alloy Segregation, Quantum Confinement and Carrier Capture in Self-Ordered Pyramidal Quantum Wires", Nano Lett. **6**, 1036-1041 (2006).

E. Pelucchi, N. Moret, B. Dwir, D.Y. Oberli, A. Rudra, N. Gogneau, A. Kumar, E. Kapon, E. Levy and A. Palevski, "Sub-meV Photoluminescence Linewidth and >106 cm2/Vs Electron Mobility in AlGaAs/GaAs Quantum Wells Grown by Metallorganic Vapor Phase Epitaxy on Slightly Misoriented Substrates", J. Appl. Phys. **99**, 093515 (2006).

E. Pelucchi, S. Watanabe, K. Leifer, Q. Zhu, B. Dwir, P. De. Los Rios and E. Kapon, "Mechanisms of Quantum Dot Energy Engineering by Metalorganic Vapor Phase Epitaxy on Patterned Nonplanar Substrates", *Nano Letters*. **7** (5), 1282-1285, 2007.

K. Leifer, E. Pelucchi, S. Watanabe, F. Michelini, B. Dwir and E. Kapon "Narrow (≈4meV) inhomogeneous broadening and its correlation with confinement potential of pyramidal quantum dot arrays", submitted.

Imperial College:

D. D. Vvedensky, "Multiscale modelling of nanostructures", *Journal of Physics: Condensed Matter* **16**, R1537-R1576 (2004).

B. A. Joyce and D. D. Vvedensky, "Self-organization of InAs on GaAs surfaces", *Materials Science and Engineering R: Reports* **46**, 127-176 (2004).

C. A. Haselwandter and D. D. Vvedensky, "Stochastic equation for the morphological evolution of heteroepitaxial thin films", *Physical Review B* **74**, 121408(R) (2006).

C. A. Haselwandter and D. D. Vvedensky, "Multiscale theory of fluctuating interfaces: Renormalization of atomistic models", *Physical Review Letters* **98**, 046102 (2007)

C. A. Haselwandter and D. D. Vvedensky, "Fluctuation regimes of driven epitaxial surfaces", *Europhysics Letters* **77**, 38004 (2007).

C. A. Haselwandter and D. D. Vvedensky, "Renormalization of stochastic lattice models I: Basic formulation", submitted to *Physical Review E*.

B. A. Joyce and D. D. Vvedensky, "Quantum dots in the InAs--GaAs system: An overview of their formation", **(invited)** in **Quantum Dots: Fundamentals, Applications, Frontiers**, edited by B. A. Joyce, P. C. Kelires, A. N. Naumovets, and D. D. Vvedensky (Kluwer, Dordrecht, 2005), pp. 1-26.

C. A. Haselwandter and D. D. Vvedensky, "From atomistic to continuum descriptions of morphological evolution", in **Modeling of Morphological Evolution at Surfaces and Interfaces**, edited by J. Evans, C. Orme, M. Asta, and Z. Zhang, *Materials Research Society Symposium Proceedings*, Vol. **859E** (Materials Research Society, Pittsburgh, PA, 2005), pp. JJ8.8.1-JJ8.8.6.

C. A. Haselwandter and D. D. Vvedensky, "Langevin equation for self-organized morphologies of thin heteroepitaxial films", **(invited)** in **International Conference on nanostructures self-assembling**, edited by I. Berbezier and M. De Crescenzi, *Surface Science* (in press).

C. A. Haselwandter and D. D. Vvedensky, "Multiscale theory of fluctuating interfaces: Renormalization and self-organization", **(invited)** in International Workshop on **Nonlinear Dynamics and Complex Systems**, edited by L. Baowen and L.-H. Tang, *International Journal of Modern Physics B* (in press).

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

Article on this project: "Mystery of quantum dots to be revealed", S. Bush, *Electronics Weekly*, January 27, 2003.

1 D. Patents and industry collaborations

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

1 F. Participation in other conferences

Please list only the most relevant

Invited Talks for EK:

E. Kapon, "Site-Controlled Quantum Dots Grown on Patterned Substrates: Physics and Applications", 13th International Winterschool on Developments in Solid State Physics: *LOW DIMENSIONAL SYSTEMS*, Mauterndorf, Province of Salzburg, Austria, February 15-20 ,2004.

E. Kapon, "Optics of Site-Controlled Quantum Nanostructures", International Quantum Electronics Conference, San Francisco, USA, May 17-21 (2004).

E. Kapon, "Seeded Self-Ordereing of Quantum Nanostructures on Patterned Substrates", From Solid State to Bio Physics II, Cavtat, Dubrovnik, Croatia, June 26 – July 2, 2004.

E. Kapon, "Site- and Energy-Controlled Semiconductor Quantum Dots for Quantum Information Processing Applications", Mini Colloquium: *Quantum Dots for Quantum Computing*, 20th CMD-EPS Conference, Prague, Czech Republic, July 19-23, 2004.

E. Pelucchi, S. Watanabe, A. Malko, M. H. Baier, K. Leifer, B. Dwir and E. Kapon " Pyramidal Quantum Dots: Seeded Self-Ordering by OMCVD on Patterned Substrates", joint ICCG-14 ICVGE-12, 14th International Conference on Crystal Growth and 12th International Conference on Vapour Growth and Epitaxy, Grenoble, France, 9-13 August, 2004.

E. Kapon, "Heterostructure Engineering on the Nanoscale: From Quantum

Wells to Quantum Dots", Summer School on *Quantum Dots: Physics and Applications*, Monte Verita, Switzerland, September 5-10, 2004.

E. Kapon, "Site- and Energy-Controlled Quantum Dots for Photonic Applications", LEOS Annual Meeting, Puerto Rico, USA, November 7-12, 2004

E. Pelucchi, S. Watanabe, K. Leifer, Q. Zhu, B. Dwir, M.H. Baier, A. Malko and E. Kapon, "MOCVD growth of III-V semiconductor ordered nanostructures (QDs) in pre-patterned inverted pyramidal recesses", session on Nano-objects at the 19th Surfaces and Interfaces Meeting (JSI 2005), Lyon, France, January 26 - 28, 2005.

E. Kapon, "Semiconductor Quantum Wires Grown on Nonplanar Substrates: Physics and Technology", 342nd Wilhelm and Else Heraeus Seminar: *Science and Technology of Inorganic Nanowires*, Bad Honnef, Germany, February 13-16, 2005.

E. Kapon, "Site-Controlled Quantum Wires and Dots Grown on Nonplanar Substrates: Physics and Applications", *13th International Symposium on Nanostructures: Physics and Technology*, Saint Petersburg, Russia, June 20-25, 2005. (Plenary)

E. Kapon, "Novel Quantum Nanostructures Grown by MOVPE on "Planar" and Nonplanar Substrates", 13th International Conference on Metallorganic Vapor Phase Epitaxy (ICMOVPE 13), Miyazaki, Japan, May 22-26, 2006.

E. Kapon, "Self-Ordering of Epitaxial Semiconductor Nanostructures on Nonplanar Substrates", Self-Organized Nanostructures (SONS) Conference, Pisa, Italy, June 29-July 1, 2006.

E. Kapon, "Pyramidal Quantum Dots and Quantum Wires Grown on Patterned Substrates", Epitaxial Growth and Fundamental Properties of Semiconductor Nanostructures, Bonassola, Italy, September 17-22, 2006.

E. Pelucchi, A. Rudra, K. Leifer and E. Kapon, « Site-controlled Single Quantum Wires and Quantum Dots Grown by MOVPE on Patterned Substrates: Self-limiting Profiles, Growth Rate Anisotropies and Precursor Decomposition », Workshop on Positioning of Single Nanostructures, Freudenstadt-Lauterbad, Germany, 2-3 November 2006.

Invited Talks for DDV:

Fourth SIAM Conference on Mathematical Aspects of Materials Science, 24-25 May 2004, Los Angeles, California

Mathematics in Nanoscale Science and Engineering, 6-11 June 2004, UCLA, Los Angeles, California

Turkish Physical Society 23rd International Physics Congress, 13-16 September 2005, Mugla, Turkey

Multiscale Modeling in Condensed Matter and Materials Science, 17-20 October 2005, UCLA, Los Angeles, California

Culminating Workshop on Bridging Time and Length Scales in Materials Science and Bio-Physics, 11-16 December 2005, Lake Arrrowhead California

International Conference on the Frontiers of Nonlinear and Complex Systems, 24-26 May 2006, Hong Kong SAR, China

International Conference on NANO-Structures Self-Assembling, 2-6 July 2006, Aix-en-Provence, France

Workshop on Epitaxial Growth and Fundamental Properties of Semiconductor Nanostructures, 17-22 September 2006, Bonassola, Italy

First non-VIRTual Meeting on "Instabilities on Surfaces", 29 September-1 October 2006, "Sunny Beach" Coast Line Resort, Black Sea, Bulgaria

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

AT EPFL:

Tim Otterburg, Ph.D. student, January to June 2004, Ph.D. awarded.

Noëlle Gogneau, Postdoc, November 2004 to September 2006.

Georg Schusteritsch, Master student, April to June 2006.

Jadaun Pryiamvada, Summer student, May to July 2006.

Dmitri Klinov, Scientist, January to May 2006.

Emanuele Pelucchi, Scientist, October 2005 to September 2006.

Dimitri Vvedensky, Visiting Professor, June 2006

At Imperial College:

Christoph Haselwandter, Ph.D. student, 10/03-9/06, Ph.D. awarded
A. dalla Volta, Ph.D. student, 10/04-8/05, no Ph.D. awarded
Dr. A. Chua, Postdoc, 4/06-12/06.

EUROPEAN SCIENCE FOUNDATION

EUROCORES Programme
European Collaborative Research

SONS
Self-Organized NanoStructures

Part 2

Final Report
of the Collaborative Research Project
"SONS-AMPHI"

Collaborative Research Project (CRP) (**to be completed with information form the ESF database**)
1. General information
Project Reference Number (): **02-PE-SONS-JA016-SONS-AMPHI** Acronym / Short Title: **SONS-AMPHI** Full Title: **Higher Levels of Self-Assembly of Ionic Amphiphilic Copolymers: Strategies Based on Multiple Molecular Interactions** Project Leader name: Dr. Axel Müller, Professor Project Leader affiliation: Makromolekulare Chemie II, Universität Bayreuth, Germany Institutional home page (URL): www.uni-bayreuth.de Project-related home page (URL): Reporting period: *from 1 January 2006*
2. Individual Projects (IPs) and Associated Partners (APs) of the Collaborative Research Project (CRP)
IP 1
Principal Investigator (name & affiliation): Prof. Dr. Axel Müller Makromolekulare Chemie II Universität Bayreuth D-95440 Bayreuth, Germany
Total Funding amount of the IP *(to be corrected by the PI):* EUR ???
IP 2
Principal Investigator (name & affiliation): Dr. Helmut Schlaad Max Planck Institute of Colloids and Interfaces (MPI-KG) Research Campus Golm, 14424 Potsdam, Germany
Total Funding amount of the IP *(to be corrected by the PI):* EUR 69,614.05

IP 3
Principal Investigator (name & affiliation): Prof. Dr. Matthias Ballauff Physikalische Chemie I Universität Bayreuth D-95440 Bayreuth, Germany
Total Funding amount of the IP *(to be corrected by the PI) :* EUR ???
IP 4
Principal Investigator (name & affiliation): Prof. Dr. Gerhard Findenegg Stranski-Laboratorium TU Berlin D-10623 Berlin, Germany
Total Funding amount of the IP *(to be corrected by the PI):* EUR ???
IP 5
Principal Investigator (name & affiliation): Dr. Martien A. Cohen Stuart, Professor Wageningen University Laboratory of Physical Chemistry and Colloid Science NL-6703 HB Wageningen, The Netherlands
Total Funding amount of the IP *(to be corrected by the PI)* 4*OIO + 20000 + additional budget
IP 6
Principal Investigator (name & affiliation): Dr. Mohamed Daoud Service de Physique de l'Etat Condensé (SPEC) CEA-Saclay, 91191 Gif sur Yvette, France
Total Funding amount of the IP *(to be corrected by the PI):* EUR ???
IP 7
Principal Investigator (name & affiliation): Dr. Avraham Halperin DRFMC/SI3M CEA-Grenoble, 17, rue des Martyrs, 38054 Grenoble Cedex 9, France
Total Funding amount of the IP *(to be corrected by the PI):* none
AP 1
Principal Investigator (name & affiliation): Dr.Oleg Borisov Institut Pluridisciplinaire de Recherche sur l'Environnement et les Materiaux, UMR 5254 CNRS/Universite de Pau et des Pays de l'Adour 2, avenue President Angot F-64053 Pau, France
AP 2
Principal Investigator (name & affiliation): Dr. Günter REITER Institut de Chimie des Surfaces et Interfaces CNRS UPR 9069 15, rue Jean Starcky, BP 2488 F-68057 Mulhouse, FRANCE

To be completed by the Project Leader of the Collaborative Research Project

3. What are the achievements of the Collaborative Research Project (CRP) (max 2 p.)

Please provide a brief overview of the most important achievements of the CRP, including
- Information on how and if the same results could have been achieved without the involvement in the CRP
- any other achievement beside the scientific results such as:
  - new directions, new ideas, new questions, new formulations, new topics for research, new thematic workshops which came out of this CRP etc

Synthesis:

A library of amphiphilic and bis-hydrophilic diblock copolymers comprising ionic (pH- sensitive), non-ionic hydrophilic and hydrophobic blocks in different combinations with well controlled and systematically varied molecular weights of blocks has been synthesized.

Experiments:

New insight has been gained on the **structure and dynamics of polyelectrolyte brushes and micelles,** in particular the questions when frozen or dynamic micelles are formed.

Higher levels of self-assembly have been studied for three systems:

- A novel type of water soluble **Inter-Polyelectrolyte Complexes (IPECs)** of **star-shaped** and **brush-like PAA** with **oppositely charged linear polyelectrolytes** forming **water-soluble micellar IPECs** in which the original copolymer micelle plays a lyophilizing part.
- A significant progress has been achieved along one of the most challenging directions of the project, i.e., preparation of asymmetric **"Janus" micelles by** exploiting the **coacervation** of pairs of **bis-hydrophilic block-copolymers** with oppositely charged ("complementary") associating blocks. Here the synergetic effect of collaboration of four groups (Wageningen, Bayreuth, Golm, and Berlin) has enabled a real breakthrough to obtain results of outstanding scientific importance. For the first time it has been unambiguously proven that disk-shaped micellar aggregates with complex coacervate core and demixed (asymmetric) corona are formed upon co-micellization of PAA-*b*-PAAm with P2VP-*b*-PEO.
- A novel Janus structure, **Janus discs**, has been achieved by crosslinking the PB block of PS-PB-PtBMA triblock terpolymers in the bulk followed by sonication.
- **Interaction of spherical polyelectrolyte brushes** (SPB) having a polystyrene latex core grafted with PSS chains **with oppositely charged surfactants** was studied. A strong binding of the hydrophobic surfactant counterions onto the anionic SPB leading to the brush size shrinkage was demonstrated.
- **Self-assembly in thin films** of diblock and star-like copolymers containing rather rigid polypeptide blocks has been investigated (Mulhouse,Golm). The formation and evolution of ordered structures on a multitude of length scales has been observed. The goal was to understand the mechanisms which are responsible for the development of highly ordered morphologies.

Theory and modelling:

- A theory was developed for the **micellization of ionic block copolymers** with pH-sensitive and hydrophobic (thermo-sensitive) blocks. The results of the SCF modelling concern pH-induced abrupt structural transformations of the micellar aggregates are in excellent agreement with predictions of the analytical theory.
- Analytical theory and molecular realistic numerical SCF modelling of **conformations and counterion distribution in polyelectrolyte stars and colloidal polyelectrolyte brushes** has been performed on the basis of the generalized Poisson-Boltzmann approach.
- A theory of conformational transitions in amphiphilic $(A_nB_m)_p$ **core-shell star-like copolymers** was developed by combining analytical and the self-consistent field (SCF) approach.
- Structural organization of **cylindrical core-shell molecular brushes** was studied by SCF and scaling theory
- The spontaneous formation of **Janus micelle**s from by $A_nB_mC_n$ triblock terpolymers in a good solvent for the A_n and C_n blocks and a poor for the middle B_m block was developed.

4. What did you not achieve in the CRP and why? (max 1 p.)

Please use the original proposal as reference and explain any deviations from the work plan

The major goals of SONS-AMPHI have been reached. The PI of AP 1 (Claudine Williams) deceased and her contribution could not be realized. Instead, Dr. Oleg Borisov (Universté de Pau) joined the project. The AP's naturally suffered from lack of funding for staff. Funding of intra-project networking was not provided. The internal structure of CEA apparently made it difficult to alot the applied funding to IP 7, maybe also IP 6.

5. Are there any follow-up activities related to the CRP and the EUROCORES Programme? (max 1 p.)

5. A. Please give details of any new research project (i.e. within FP7, COST Action, etc) or any spin-off company that was developed as a result of the collaboration of the CRP and the EUROCORES Programme (short-term strategies- next 2/3 years)

Part of the IP and AP of SONS-AMPHI and NEDSPE takes part in SONS II with funded project BIOSONS.
The follow up of the research carried in the framework of the Eurocores programme is contained in a new research proposal for the EU FP7 (coordinated by the Wageningen group).

5. B. Please give recommendations for future developments of the area and research priorities to ESF and to Funding Agencies (long-term strategies-next 5/10 years)

6. Your feedback on the EUROCORES Programme (max 1 p.)

6.A. What, in your view, is the added value of being part of a EUROCORES Programme

6.B. Give any critical and constructive comments on the EUROCORES Programme and its procedures

It would be highly welcome if the all national funding agencies (e.g. CNRS) would consider contributing in a more direct and quality-oriented fashion to the EUROCORES activities.

Appendix 1. List of Products of the CRP

1 A. Joint publications and products

Please include only those resulting from the **joint work of two or more** CRPs (if any)

I.K. Voets, A. de Keizer, P. de Waard, P.M. Frederik, P.H.H. Bomans, H. Schmalz, A. Walther, S.M. King, F.A.M. Leermakers, M.A. Cohen Stuart, "
Double-faced micelles from water-soluble polymers" ,
Angew. Chem. Int. **45** (2006) 6673-6676.

Voets, I.; de Keizer, A.; Cohen Stuart, M.; Justynska, J.; Schlaad, H.
"Irreversible structural transitions in mixed micelles of oppositely charged diblock copolymers in aqueous solution",
Macromolecules **2007**, *40 (6)*, 2158-2164.

M. Ballauff, M. Patel, S. Rosenfeldt, N. Dingenouts, T. Narayanan, A.H.E. Müller, and F. Plamper
Analysis of the correlation of counterions to macroions by anomalous small-angle scattering
Polym. Mater. Sci. Eng. **93,** 232 (2005)

F. A. Plamper, H. Becker, M. Lanzendörfer, M. Patel, A. Wittemann, M. Ballauff, A. H. E. Müller
Synthesis, Characterization and Aqueous Solution Behaviour of Star-shaped Poly(acrylic acid)
Macromol. Chem. Phys. **206,** 1813 (2005)

F. A. Plamper, A. Walther, A. H. E. Müller, M. Ballauff
Nanoblossoms: Light-Induced Conformational Changes of Cationic Polyelectrolyte Stars in Presence of Multivalent Counterions
Nano Letters **7**, 167 (2007)

F. A. Plamper, A. Schmalz, E. Penott-Chang, M. Drechsler, A. Jusufi, M. Ballauff, A. H. E. Müller
Synthesis and Characterization of star-shaped Poly(N,N-dimethylaminoethyl methacrylate) and its corresponding quaternized ammonium salts
submitted to *Macromolecules*

Structure Formation of Polystyrene-block-poly(γ-benzyl L-glutamate) in Thin Films;
S. Ludwigs, G. Krausch, G. Reiter, M. Losik, M. Antonietti, H. Schlaad,
Macromolecules, 38, 7532 (2005)

I. Botiz, N. Grozev, H. Schlaad, G. Reiter,
Processes of Pattern Formation in Swollen Thin Films of Polypeptide Block Copolymers; submitted to EPJE

I. Botiz, H. Schlaad, G. Reiter (in preparation)
The Influence of Water on Processes of Pattern Formation in Swollen Thin Films of Polypeptide Block Copolymers,

1 B. Publications and products of individual projects

Please include only those resulting from research carried out **within the CRP (both joint and individual)**

K. Loos, A. Böker, H. Zettl, M. Zhang, G. Krausch, A. H. E. Müller
Micellar Aggregates of Amylose-*block*-Polystyrene Rod-Coil Block Copolymers in Water and THF
Macromolecules, **38**, 873 (2005)

X. André, M. Zhang, A.H.E. Müller
New Thermo- and pH-Responsive Micelles of Poly(acrylic acid)-block-Poly(N,N-diethylacrylamide)
Macromol. Rapid Commun. **26**, 558 (2005)

P. Petrov, M. Bozukov, M. Burkhardt, S. Muthukrishnan, A. H.E. Müller, Ch. B. Tsvetanov
Stabilization of polymeric micelles with mixed poly(ethylene oxide)/poly(2-hydroxyethyl methacrylate) shell by formation of poly(pentaerythritol tetraacrylate) nanonetworks within the micelles
J. Mater. Chem. **16,** 2192 (2006)

E. Eghbali, O. Colombani, M. Drechsler, A. H. E. Müller, H. Hoffmann
Rheology and Phase Behavior of Poly(n-Butyl Acrylate)-block-Poly(Acrylic Acid) in Aqueous Solution
Langmuir **22**, 4766 (2006)

A. Walther, X. André, M. Drechsler, V. Abetz, A. H. E. Müller
Janus Disks
J. Am. Chem. Soc. **129** (2007), published online on April 19, 2007

O. Colombani, M. Ruppel, F. Schubert, H. Zettl, D.V. Pergushov, A.H.E. Müller
Synthesis of Poly(n-butyl acrylate)-block-Poly(acrylic acid) Diblock Copolymers by ATRP and Their Micellization in Water
Macromolecules,**40** (2007) published on the internet on May 16, 2007

O.Colombani, M.Burkhardt, M. Drechsler, M. Ruppel, M. Schumacher, A. H.E. Müller
Structure and Dynamics of Micelles of Poly(*n*-butyl acrylate)-*block*-Poly(acrylic acid) Diblock Copolymers in Aqueous Solution
Macromolecules, **40** (2007) published on the internet on May 16, 2007

Justynska, J.; Hordyjewicz, Z.; Schlaad, H.
"New functional diblock copolymers through radical addition of mercaptans",
Macromol. Symp. **2006**, *240*, 41-46.

Geng, Y.; Discher, D.E.; Justynska, J.; Schlaad, H.
"Grafting short peptides onto polybutadiene-*block*-poly(ethylene oxide): A new platform for self-assembling hybrid amphiphiles",
Angew. Chem. Int. Ed. **2006**, *45 (45)*, 7578-7581.

P.S. Hofs, I.K. Voets, A. de Keizer, M.A. Cohen Stuart,
"Comparison of complex coacervate core micelles from two diblock copolymers or a single diblock copolymer with a polyelectrolyte"
Physical Chemistry Chemical Physics **8** (**36**) (2006) 4242-4251.

I.K. Voets, A. de Keizer, M.A. Cohen Stuart, P. de Waard
"Core and corona structure of mixed polymeric micelles"
Macromolecules **39**(17) (2006) 5952-5955.

M.A. Cohen Stuart, P.S. Hofs, I.K. Voets, A. de Keizer
"Assembly of polyelectrolyte-containing block copolymers in aqueous media
" Curr. Opin. Coll. Interf. Sci. **10** (2005) 30-36.

Jens-Uwe Sommer and Günter Reiter;
Morphogenesis and non-equilibrium pattern formation in two-dimensional polymer crystalliza-

tion;
Phase Transition, 77, 703-745 (2004)

Leonid V. Govor, Günter Reiter, Gottfried H. Bauer and Jürgen Parisi;
Nanoparticle ring formation in evaporating micron-size droplets;
Appl. Phys. Lett. 84, 4774-4776 (2004)

Günter Reiter;
Deriving Molecular Parameters of Interfaces Between Chemically Identical Polymers from Macroscopically Observed Phenomena;
Macromol. Symp. 229, 81–92 (2005)

F. Vonau, D. Suhr, D. Aubel, L. Bouteiller, G. Reiter and L. Simon;
Evolution of multilevel order in supramolecular assemblies;
Phys. Rev. Lett. 94, 066103 (2005)

F. Vonau, D. Aubel, L. Bouteiller, G. Reiter, L. Simon,
Cooperative re-arrangements leading to long range order in monolayers of supramolecular polymers;
submitted to Phys. Rev. Lett.

G. Reiter, I. Botiz, L. Graveleau, N. Grozev, K. Albrecht, A. Mourran, M. Möller,
Morphologies of Polymer Crystals in Thin Films;
in: Lecture Notes in Physics: Progress in Understanding of Polymer Crystallization, Springer, Berlin Heidelberg, 714, 179-200 (2007)

1 C. General outreach

Radio interviews, TV coverage, Newspaper articles etc.

1 D. Patents and industry collaborations

1 E. Networking within the CRP

Networking with other CRPs is in Part 3 (completed by ESF)

Both the intra- and inter-project collaboration has been strengthened by multiple bi-, tri-, and multilateral collaborations (see in particular Janus project with its synthetic, experimental and theoretical interaction).

A number of workshops have taken part, in particular together with AMPHI and NEDSPE (Archachon, Prague) which has led to the successful application of BIOSONS in the SONS II call. Another workshop with SPENSA, SISAM and NETSOMA will take place in Bristol, June 07. In addition, we profited from the general SONS meetings in Strasbourg and Pisa.

More bilateral collaborations with other SONS projects have been established, e.g. between Günter Reiter and Mario Ruben (FunSMART).

Presentations at major SONS activitities:

A.H.E. Müller, “Janus Micelles”, SONS Conference 2006, Pisa/Italy (2006)

M.A. Cohen Stuart: “Self-organized nanostructures” SONS Conference 2006, Pisa/Italy (2006)

H. Schlaad: “Toolbox of amphiphilic polymers and complex assemblies”, SONS Conference 2006, Pisa/Italy (2006)

H. Schlaad: “New functional polymers and biohybrids through modification of polybutadienes”, SONS Networking Activity Workshop, Prague/Czech Republic (2006)

I. Botiz, G. Reiter, H. Schlaad ; SONS Workshop “Structure and properties of self-organized amphiphilic copolymers”, 4-7th of October 2006, Prague (Czech Republic)

I. Botiz, N. Grozev, G. Reiter, H. Schlaad; Self-Assembly of Star-Block Copolymers Containing Polypeptides in Thin Films, Polyamphi Meeting, 6-7th of April 2006, Murten (Switzerland)

G. Reiter; Processes of Self−Assembly of Polymers in Thin Film; Workshop “Self-assembled Structures of Amphiphilic Ionic Copolymers in Solutions and at Interfaces”, May 11-14, 2005, Arcachon (France)

1 F. Participation in other conferences

Please list only the most relevant

H. Schlaad: ”Hydrophilically modified polybutadienes: Synthesis and solution properties”, Polymers & Coatings 2006, Mainz/Germany (2006)

9-16, 2006, Prague (Czech Republic)

Polymers in Confined Geometries: Interfacial Phenomena; G. Reiter; 1st French-Brazilian Polymer Meeting, April 24 - May 1, 2005, Florianopolis (Brazil), Processes of Structure Formation of Block Copolymers Containing Polypeptides; I. Botiz, G. Reiter, H. Schlaad; COST P12 Conference “Crystallisation and Structure Formation of Polymers” 8-11th of October 2006, Mittelwihr (France)

Morphologies of Polymer Crystals in Thin Films, G. Reiter; 1st China-France Bilateral Workshop on Polymer Crystallization; 06-09/06/2006, Nanjing, China

Morphologies of polymer crystals in thin films; G.Reiter, Fundamental and Applied Macromolecular Science: Toward Next Generation Materials; 29 –31/01/2007, Strasbourg, France

Appendix 2. Scientific & technical personnel involved in the CRP

Personnel directly funded by the EUROCORES Programme

Please supply only the missing information stating name, position, contract start/end dates and in case of students say if they achieved a PhD

IP 1: Markus Burkhardt, 01/10/2003 – 30/09/2006

IP 2: Justyna Justynska, 01/10/2003 – 30/09/2005

Anja Gress, 01/02/2006 – 31/01/2007

IP 3:

IP 4:

IP 5: Ilja Voets, PhD student, 01/05/2004 – 01/05/2008

IP 6: Dr. Oleg Borisov, scientist,

IP 7: Dr. Oleg Borisov, scientist,