





SONS NEWS

The newsletter of the EUROCORES Programme in Self-Organised NanoStructures (SONS)

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SONS – Second Call for proposals

Following agreement with funding bodies from Austria, Belgium, Czech Republic, Germany, Ireland, Italy, Lithuania, Norway, Poland, Slovakia, Spain, Switzerland, Turkey and the United Kingdom, the European Science Foundation recently published a second call for outline proposals for collaborative research projects to be undertaken within the EUROCORES programme SONS.

After little more than a year since the first SONS conference in Strasbourg, SONS research projects and programme networking activities are starting to bear fruit. However, if Europe is to maintain its internationally competitive role in nanotechnology a strong effort is still required to coordinate European national activities in the field of SONS. For this reason, 14 of the 21 funding agencies participating in the first call plus 2 new agencies – not previously involved – have decided to join the second phase of the EUROCORES programme on SONS.

According to the standard EUROCORES scheme, the new phase of the programme will include national research funding and a European networking component.

The aims and scientific scope of the second call are inspired by the original spirit and goals of the SONS programme and are thus very close to those of the first call. The second call aims to further contribute to establish a truly *interdisciplinary* approach in the field of Self-Organised NanoStructures, engaging the best scientists and expertise available in Europe. Priority is again given to molecular self-assembly, focusing on soft and/or supramolecular matter in connection with the mechanisms, functions and fabrication of SONS. SONS proposals will be selected in a two-stage selection process: an outline proposal stage and a full proposal stage. The call for outline proposals was closed on 23 June 2005. The SONS Review Panel, formed by experts in the field, met on 26 and 27 July and decided to recommend 24 proposals to pass to the full proposal stage. ESF informed all applicants of the decision concerning their proposals on 3 August. The deadline for submission of full proposals is 3 October, 2005.

Preparing for SONS Conference 2006

The SONS Scientific Committee launched the preparations for a SONS programme science event in 2006. The purposes of the conference, focused on the science topics covered by the SONS programme, will be to serve as a showcase of the main scientific achievements of SONS projects and to provide a platform for discussion and exchange of ideas.

The Scientific Committee, formed by the project leaders as representatives of all SONS project members, held its annual meeting in Strasbourg on 30 May 2005.

One of the main issues dealt with at the meeting was the planning of *SONS Conference 2006*. The event, which will take place in Pisa in June 2006, will be essentially oriented to the SONS community and will especially foster the active participation of young SONS project members. However, as with all SONS networking activities, the *SONS Conference 2006* will be open for attendance of external participants. In particular, a few selected high-profile external experts will be invited to present plenary lectures.

The Executive Group of the Scientific Committee will be responsible for the scientific organisation of the event while the ESF will be in charge of the administrative and practical arrangements in coordination with the local organiser, Dr Alessandro Fortunelli.

Besides this general SONS science event, the Committee decided that three smaller networking activities would be organised in the period from October 2005 to September 2006.

The Committee also elected the new membership of the Executive Group of SONS:

- Silvio Decurtins (NANOSYN)
- Karen Edler (SPENSA)
- Charl Faul (SISAM)
- Dag Hanstorp (SPANAS)
- Petr Stepanek (AMPHI)
- Marcus Textor (NANO-SMAP)

Election of members for the next term will take place at the next annual meeting.

The next annual Scientific Committee meeting will take place in conjunction with the conference in Pisa in June 2006 (exact date to be confirmed).

SONS networking activities

Recently held events

• A workshop on "**Self-assembled structures of amphiphilic ionic copolymers**", convened by Dr Olivier Diat, Dr Oleg Borisov and Dr Günter Reiter, took place in Arcachon, France, from 11 to 14 May 2005. The aim of the workshop was to present the most comprehensive overview on self-assembly of amphiphilic inonic/nonionic in aqueous environment, and to identify the most challenging problems and links between fundamental research and particular nanotechnological applications.

• A workshop on "**Transport through Single-Molecules**", organised by Professor Jan M. Van Ruitenbeek and Professor Nicolas Agraït, was held from 9 to 12 March 2005 in Leiden, The Netherlands. The meeting combined two goals: (1) to serve as a platform to bring together three projects of the SONS programme – SASMEC, NANOSYN, and FUN-SMARTs; and (2) to provide an opportunity for open discussion of directions of research in this new field, and an introduction into the field for PhD students. The workshop was attended by 59 registered participants from nine countries.

• A workshop on "**Surface Nano-patterning**" organised by Dr. Alessandro Fortunelli, took place from 30 June to 1 July 2005 in Pisa, Italy. The focus of the conference was the development and characterisation of novel nanostructured interfaces that can interact specifically with inorganic and biological systems to produce systems exhibiting technologically relevant properties. This workshop aimed at training the PhD students within the SONS programme by introducing them to existing technologies for the creation and characterisation of technologically relevant, nanostructured surfaces.

• A school on **"Self-organised nanostructures"**, convened by Professor Enrique Ortega was held in Cargese, Corsica, from 18 to 23 July 2005. This summer school intended to review the state-ofthe-art and the current developments in the field of self-organisation and physical properties of self-assembled nanostructures. The school was particularly addressed to PhD students and young researchers who are entering the field.

• A combined workshop-summer school on "**Physics of living** organisms, from single molecules to networks", convened by Dr Jesper Glückstad, took place in Humlebaek, Denmark, from 21 to 28 August 2005. The workshop focused on state-of-the-art optical techniques used to manipulate and monitor the motion of biological specimen, from the single-molecule to the cellular level, such as force-scope and multiple beam optical tweezers, and the use of these to uncover fundamental aspects of biological specimen.

Upcoming events

• Three SONS workshops will be organised in 2006, details still to be defined.

• A SONS Programme Conference will be organised in June 2006 in Pisa (see dedicated article in this issue of *SONS News*).

Further information and, particularly, the links to the local websites of these events are accessible from **www.esf.org/sons.**

MOL-VIC

he self-assembly of molecules on solid surfaces is a complex phenomenon resulting from the delicate balance between thermodynamics and growth kinetics. Tailoring structures with the desired morphology and properties demands the highest control of the whole process; that is., developing the ability to synthesize and manipulate the different materials at the atomic scale, as well as acquiring the fundamental understanding of both nanoscopic interactions and emerging properties. The MOL-VIC project is a surface science approach to self-assembly, namely molecular beam epitaxy of specifically designed molecules on crystalline substrates and characterisation by powerful techniques, such as scanning tunnelling microscopy/spectroscopy and high resolution, angle-resolved photoemission. The defining feature of MOL-VIC is the use of vicinal surfaces with onedimensional (1D) arrays of steps as patterned substrates, in order to force the nanoscopic units of the system (molecules or clusters) into nano- and mesoscopic 1D (wires and stripes) periodic configurations.

The use of a wide variety of molecule and substrate combinations provides opportunities to tailor and fine-tune the system geometry and the electronic properties. To achieve 1D molecular assemblies we are designing new molecules that are likely to line up forming linear hydrogen bonding in the presence of 1D templates. One example is the benzodiguanamine molecule shown in the left panel of Fig. 1, which has been synthesized for this project. On the other hand, the chemical nature of the substrate and the growth conditions are the fundamental parameters to control

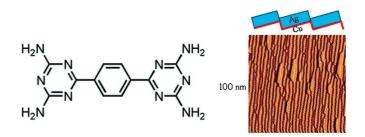


Fig. 1: Left, benzodiguanamine, specifically designed to form one-dimensional assemblies on vicinal surfaces via H-bonding. Right, STM topography from a Cu(111) vicinal surface modified with a Ag buffer layer, thereby leading to a one-dimensional density of states at the Fermi energy.

growth kinetics and system energetics. At a vicinal surface one also can vary the step density and the orientation in order to further influence surface kinetics; for example via different diffusion barriers at step edges, and via energetics, by modifying the surface energy with the elastic field of the step array or with the surface electronic structure. In MOL-VIC we are using a varied collection of vicinal crystalline substrates, from semiconducting (Si, Ge) to noble metals (Ag, Au, Cu), as well as studying adsorbate modified templates, such as Ag/Cu or Ag/Au, to provide a full range of geometries (stepped, faceted, kinked) and surface electronic states.

Of particular importance to modulate system interactions (molecule-molecule and substrate-molecule) is the ability to tune the surface electronic structure. This can be tested using noble metal substrates as model systems because these surfaces posses a high density of surface states near the Fermi energy. Indeed, both sur-

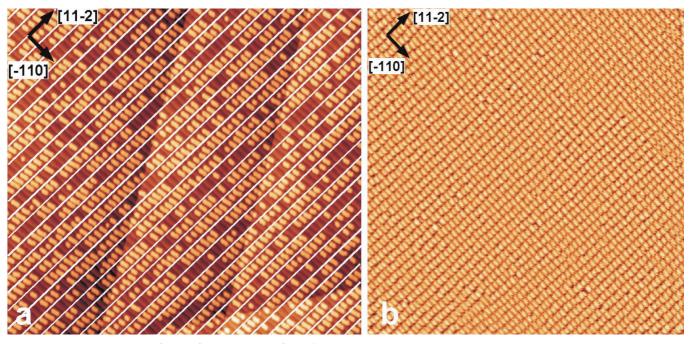


Fig. 2: STM image (200 x 180) nm² of 0,1ML of C₆₀ on Au(788) surface. White lines running perpendicular to the step edge [-110] direction are equally spaced (7,2 nm) and serve as guide for the eyes. STM image (290 x 290) nm² of 0,5 ML of C₆₀ on Au(788) surface.

face electron density and dimensionality are strongly modified in a vicinal surface. The key feature is the repulsive electron potential that characterises step edges, which results in quantum-size effects in step arrays. Thus, by manipulating the step potential and the step density it is possible to modify the surface state dimensionality and the electron level occupation. Deeper changes in the electronic structure are achieved in adsorbate-modified templates, such as the one shown in Fig. 1, right. An Ag buffer layer is grown on vicinal Cu(111), such that the step periodicity of the substrate matches the Ag layer Moiré lattice. This process replicates the step array at the surface while transforming the electronic structure from a 2D surface band with a relatively high electron occupation (clean substrate) into a 1D surface band with lower electron density (Ag layer).

The 1D anisotropy of vicinal surfaces can force single domains of surface layer reconstructions in a few-micron scale. This is particularly attractive for template fabrication. In other cases, surface reconstructions influence the equilibrium shape of the vicinal surface, leading to sharply defined, ordered patterns that also serve as growth templates. One example is Au(788), which is vicinal to the Au(111) surface, and it is characterised by a periodic fcc/hcp packing along step edges, reminiscent of the herringbone reconstruction in the (111) plane. As shown in Figure 2, C_{60} molecules preferentially adsorb at the face-centred cubic (fcc) domains of the reconstruction. At half monolayer (ML) coverage we obtain a highly periodic C_{60} nanomesh on this surface. This nanomesh exhibits an extraordinarily long-range periodicity (extending over several hundreds of nanometres), an extremely low defect density. In summary, MOL-VIC is a surface science approach to the synthesis and full characterisation of 1D supramolecular structures self-assembled on vicinal surfaces and derived 1D templates.

The **MOL-VIC** project is led by Dr José Enrique Ortega (Universidad del País Vasco, Spain).

The other partners in this project are:

Professor Richard Berndt (Christian-Albrechts-Universität Kiel, Germany), Professor Enrique Garcia Michel (Universidad Autonoma de Madrid, Spain), Professor Karsten Horn (Fritz Haber Institut of the Max Planck Society, Germany), Dr Christian Joachim, Centre for Materials Elaboration and Structural Studies, CNRS, France), Dr André Gourdon (Centre for Materials Elaboration and Structural Studies, CNRS, France).

SONS NETSOMA – Nanoscale Electrical Transport in Self-Organised Molecular Assemblies (NETSOMA)

Participating partners:

• Professor Rene Janssen/Professor Bert Meijer (Technical University of Eindhoven, The Netherlands)

• Professor Paul. Smith/Dr. Natalie Stutzmann (ETH Zürich, Switzerland)

• Dr Martin Nielsen (Risø National Laboratory, Denmark)

• Professor Henning Sirringhaus (Coordinator), Professor Richard Friend (University of Cambridge, UK)

he vision of bottom-up nanotechnology to fabricate, in a controlled manner, functional nanostructures by molecular self-assembly is currently hampered by the inability to define controlled 3-dimensional structures over sufficient length scales. Many approaches to self-organisation controlled structure formation are possible only on a length scale <10-100 nm. Block copolymers might allow controlling assembly over several different length scales. When the segments have a well-defined and, importantly, monodisperse degree of polymerisation the characteristic length scales can be controlled precisely. The intrinsic tendency of each segment in block copolymers to aggregate in an individual phase provides a means of creating a range of wellordered nanoscale morphologies (for example spheres, cylinders, lamellae) depending on the relative volume fractions. While this principle has been used in various engineering materials to create fascinating architectures, the use of block copolymers in conjugated polymers with electronic functionality has received little attention up to now and has suffered from synthetic difficulties in producing true polymers: conjugated block copolymers with high molecular-weight and small polydispersity.

The SONS NETSOMA project is focused on exploring new electronic and optical phenomena arising in well-defined nanoscopic self-assemblies of bi-functional conjugated block copolymers. The project brings together four internationally leading groups with complementary expertise in conjugated polymer synthesis (Technical University of Eindhoven), polymer processing (ETH Zürich), structural characterisation of polymers (Risø National Laboratory) and conjugated polymer materials and device physics (University of Cambridge). The methodology of the project enabled by the international SONS scheme is based on a very close collaboration of the four partners. Polymers synthesized in Eidhoven are passed on to ETH Zürich for development of the processing technique to produce large-scale, ordered microstructures, which are then characterised by the Risø team using X-ray diffraction. The Cambridge group develops new nanoscale device architectures based on their unique optical and electronic properties.

The focus of the project in the first year has been on developing truly polymeric di-block and tri-block copolymers (as opposed to oligomeric model systems) comprising a first block of

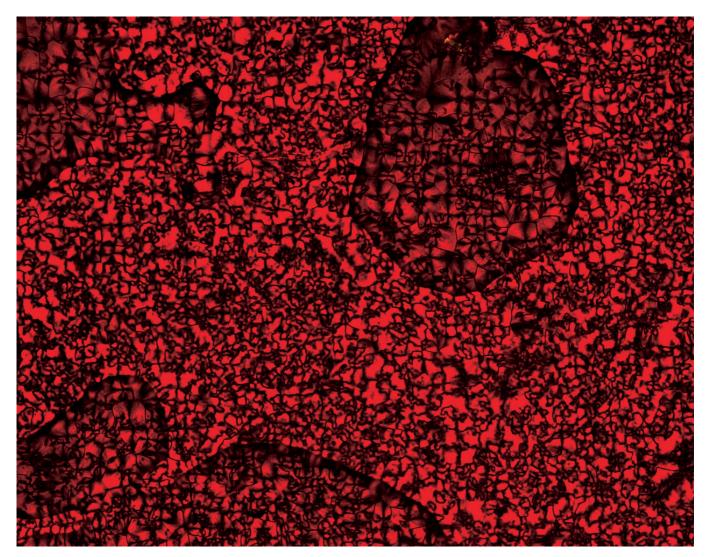


Fig 1: Polarised optical micrograph of spherullitic microstructure of polythiophene-dielectric block copolymer

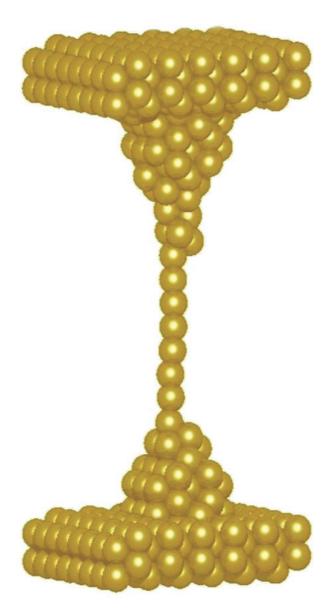
a conjugated polymer semiconductor (polythiophene) and a nonconjugated dielectric block. These polymers are of interest as model systems as well as in applications in organic field-effect devices. Initially, several routes to block copolymer synthesis were explored, based on growing the second block off the end of the first one, or on coupling two high molecular weight polymers together through appropriately functionalised end groups. The former approach has been found to be best suited, and a first generation of polythiophene-dielectric block copolymers with high molecular weight has now been synthesized successfully. We are currently developing processing techniques for the preparation of highly ordered thin films of these materials. Their properties are being characterised by X-ray diffraction as well as by optical and electrical measurements (Fig.1). During the first year of the project the partners not directly involved in the synthesis had focused on characterising the properties of polythiophene, and the dielectric polymers separately, for example by studying the properties of solution processed interfaces between the two polymers, and the knowledge gained from these studies is now being applied effectively to the block copolymer system.

A second direction which is being pursued is the study of hydrogen-bonded model oligomers based on oligo(*p*-phenylenevinylene), thiophene-perylene bisimide and quadruple hydrogen-bonded oligofluorenes. Thin-film field-effect transistors have been demonstrated with hydrogen-bonded supramolecular active layers.

The EUROCORES SONS scheme provides an excellent vehicle for this focused and interdisciplinary international collaboration which is necessary in order to surmount the considerable scientific challenges which have to date prevented long-range ordered structures and useful devices being fabricated with conjugated block copolymers. We gratefully acknowledge the support of the ESF and of the contributing research councils for this very useful initiative.

The **NETSOMA** project is led by Dr Henning Sirringhaus (University of Cambridge, United Kingdom). The other partners in this project are: Professor Richard H. Friend (University of Cambridge, United Kingdom), Professor Rene A.J. Janssen (Eindhoven University of Technology, The Netherlands), Professor Egbert W. Meijer (Eindhoven University of Technology, The Netherlands), Dr Martin M. Nielsen (Risøe National Laboratory, Denmark), Dr Klaus Bechgaard (Risoe National Laboratory, Denmark), Professor Paul Smith (Swiss Federal Institute of Technology in Zürich, Switzerland).

The SASMEC project



Inspired by an early paper by Aviram and Ratner (*Chem. Phys. Lett.* **29**, 277 [1974]) many have speculated about the possibility of building electronic devices using organic molecules as the elementary components of the circuits. Various experimental approaches have been developed since to apply electrical contacts to individual organic molecules and investigate their properties. Although some believe that practical devices may be realised soon, there is hardly any understanding of the actual atomic-scale configuration of the devices and quantitative comparison with theory has shown to be elusive. The SASMEC project combines teams of chemists, experimental physicists and computational physicists aiming to tackle this outstanding fundamental problem by gradually developing our knowledge through carefully selected simple model systems.

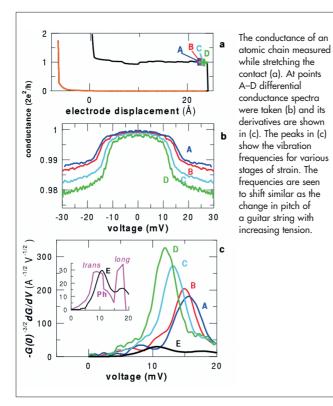
The simplest model systems are single atom contacts and atomic chains of single metal atoms. The chains self-assemble during controlled rupture of the metals gold, platinum or iridium and they constitute the ultimate nanowires. The atomic-sized conductors have highly unusual electronic and mechanical properties. For example, atomic chains are able to sustain enormously large current densities, the bonds are stronger by about a factor of three compared to bulk bonds, and they are highly reactive towards many atomic and molecular species even when the chain is composed of noble metal gold. In recent years we have gained insight into the conduction mechanism and the stability of these systems. The techniques used to form them are based on STM or mechanically controllable break junction instruments. The experiments are often performed at low temperatures that greatly improve our ability to characterise the system, keep it stable and avoid contamination.

Chains up to seven atoms can be formed in this way. We believe that much longer chains could be formed if we could have more control over the process. To this end we want to employ an ultra-high vacuum low-temperature STM set-up that we are developing. Some of the questions that remain to be answered are: what are the elementary processes by which electrons lose their energy to the ions in the chain, and how is this energy transmitted to the electrodes? Can we incorporate foreign atomic or molecular species into the chains and thereby stabilise them further?

The concepts and insight developed in the study of atomic contacts and chains are valuable in taking the next step, where we want to contact individual molecules using similar techniques. The Leiden group has recently demonstrated the principles on the simplest model molecule: a conducting bridge of a single hydrogen molecule. By employing vibration spectroscopy and other low-temperature emethods we have been able to obtain convincing evidence that a single H₂ molecule was contacted and the Denmark team has obtained nearly quantitative agreement with model calculations for this system. This result now provides a benchmark for model calculations and it forms our starting point to gradually extend the investigations towards more elaborate molecular objects. First results, both experimentally and computationally, have been obtained for carbon monoxide and work is under way on acetylene, H2S, and more. We will concentrate initially on simple molecules that are easy to handle experimentally and computationally.

Ultimately, when approaching the molecules of interest for applications we need to employ chemistry at room temperature to bind the molecules to the metal electrodes. The standard approach is using thiol groups to bind to gold. In a parallel effort the Madrid team investigates single dithiol molecules in a self-assembled monolayer of inert thiols and then attaches gold nanoclusters to their free end. The nanocluster is then contacted using a low temperature AFM/STM.

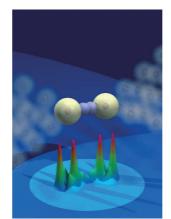
Development of new research tools forms an important part of our research efforts. As one of the tools, we are focusing on force sensors based on quartz tuning fork resonators. The sensors are



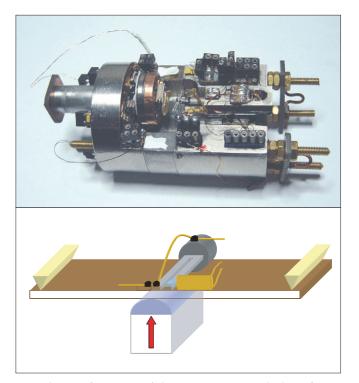
exploited for AFM scanning applications on self-assembled monolayers of molecules, but they have also been incorporated into mechanically controllable break junction devices in order to measure the forces while stretching junctions of single molecules. On the computational side the Denmark team has developed and maintains a plane-wave code for Density Functional Theory using ultrasoft pseudopotentials. A new method was recently developed for calculations of the electronic structure and forces on atoms in the presence of an electric current.

We are part of a world-wide effort for which we expect to see a significant breakthrough soon. We feel privileged to be able to contribute to these exciting developments.

The **SASMEC** project is led by Professor Nicolás Agrait (Universidad Autonoma de Madrid, Spain). The other partners in this project are: Professor Jan van Ruitenbeek (Leiden University, The Netherlands), Professor Mads Brandbyge (Technical University of Denmark), Dr Marisela Vélez (Universidad Autónoma de Madrid, Spain), Professor Karsten Wedel Jacobsen (Technical University of Denmark).



Structure of a junction formed by a single hydrogen molecule between platinum electrodes, as derived from experimental evidence. The graph below shows the distribution of electronic states.



Two applications of quartz tuning fork resonators in our research. The top figure shows an AFM with the tuning fork as the force sensor. The lower panel shows a schematic diagram of a break junction instrument incorporating a tuning fork force sensor that will allow us to measure single-molecule junctions.



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- Belgium Fonds National de la Recherche Scientifique (FNRS) [1]
- Belgium Fonds voor Wetenschappelijk Onderzoek Vlaanderen (FWO) [1,2]
- Czech Republic Grantovà agentura České republiky [1,2]
- Denmark Statens Naturvidenskabelige Forskningsråd (SNF) [1]
- Finland Suomen Akatemia/Finlands Akademi [1,2]
- France Commissariat à l'Energie Atomique/Direction des Sciences de la Matière (CEA) [1]
- Germany Deutsche Forschungsgemeinschaft (DFG) [1,2]
- Hungary Országos Tudományos Kutatási Alapprogramok (OTKA) [1]
- Hungary Magyar Tudomanyos Akademia [1]
- Ireland Enterprise Ireland [1,2]
- Ireland Irish Research Council for Science, Engineering and Technology (IRCSET) [2]
- Italy Consiglio Nazionale delle Ricerche (CNR) [1,2]
- Lithuania Lithuanian State Science and Studies Foundation [2]
- The Netherlands Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) [1]
- Norway Norges Forskningsråd [1,2]
- Poland Polska Akademia Nauk (PAN) [1,2]
- Portugal Fundação para e Ciência e a Tecnologia (FCT) [1]
- Slovakia Slovak Academy of Sciences [1,2]
- Spain Consejo Superior de Investigaciones Científicas (CSIC) [1,2]
- Spain Ministerio de Educación y Ciencia (MEC) [1,2]
- Sweden Vetenskapsrådet [1]
- Switzerland The Swiss National Science Foundation for the Promotion of Scientific Research [1,2]
- Turkey Scientific and Technical Research Council of Turkey (TÜBITAK) [1,2]
- United Kingdom Engineering and Physical Sciences Research Council (EPSRC) [1,2]
- [1,2]: Agencies participating in the first and second call
- [1]: Agencies participating only in the first call
- [2]: Agencies participating only in the second call

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