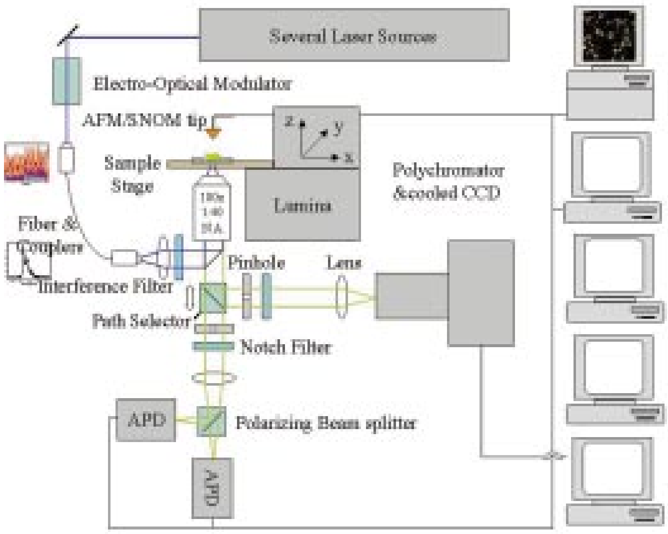
Structuring, Manipulation, Analysis and Reactive Transformation of Nanostructures (SMARTON)

An ESF scientific programme



Nanostructures are built bottom up from molecules interconnected by non-covalent inter-molecular bonds, and have a wide variety of applications, for example in the plastics industry and catalysis. The study of nanostructures is an extension of supramolecular chemistry, which deals with complex compounds created by non-covalent bonds between existing molecules, as opposed to simple compounds comprising atoms linked by covalent bonds.

Supramolecular chemistry has been exploited in a variety of industrial processes for many years, but until recently it has not been possible to analyse and manipulate these structures at the submicron level. With scanning probe microscopy it is now possible to resolve structures down to the level of single molecules, and this brings with it the potential to attain a much deeper understanding of the processes by which molecules are assembled into larger structures. The next step is to develop tools to both investigate these processes and start manipulating the structures to change their mechanical and chemical properties. Then it is possible to start developing novel nanoscale structures with potential for practical applications.

The aim of the SMARTON scientific programme is to develop the necessary understanding and tools, and then to proceed to design and assemble some new nanoscale systems, including switches, molecular engines, and dendritic structures, the latter being molecular arrays or tree like structures suitable for building large complex molecules.

The programme is split into three branches covering the different types of supramolecular structure: - organic, inorganic and polymer. These three branches started with independent aims and objectives but with strong interaction and sharing of some methods. The three branches also have the common final goal of designing nanoscale systems with new properties.

Introduction

A variety of new techniques such as scanning probe microscopy and nanomanipulation have brought science to the brink of being able to construct and manipulate a variety of structures at the level of individual molecules. The aim of this programme is to take these existing techniques, extending them where necessary, and then apply them to the organisation, analysis, manipulation and transformation of organic, metallo-organic, zeolite based hybrid systems, and macromolecular structures. The feasibility of "seeing" what is happening at the molecular level was demonstrated recently by the use of STM (scanning tunnelling microscopy) to obtain images of a photochemical transformation or in the expanding field of single molecule spectroscopy. Then the feasibility of manipulating very small structures of sub-micron dimensions was demonstrated by bleaching a single latex particle in an ensemble of particles, using a Scanning near field optical microscope.

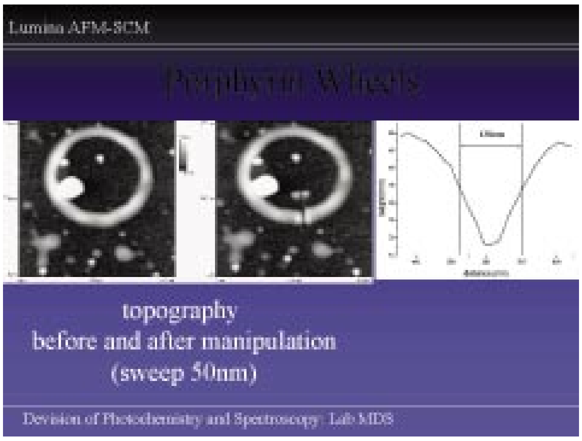
This programme is building on these early developments by combining the efforts of research groups that are already at the forefront of their respective domains. This is bringing together the three inter-related domains of organic, inorganic and polymer based research, and the combination of these fields is yielding some new ways of building structures via highly controlled nanochemistry.

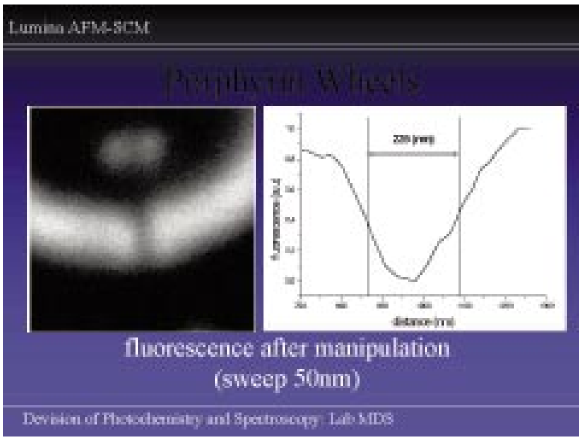
In particular SMARTON aims to create a second generation of nanoscale systems by making progress on the following three fronts:

1 ▪ Understanding the different factors influencing organisation in two and three dimensions of specifically designed structures, either at a surface or in solution.

2 ▪ Understanding the relation between structure and reactivity of these specifically designed structures.

3 ▪ Using new and existing methodology to manipulate, study and quantify, at the submicron level, changes in properties induced either by irradiation or electrical stimulus.





Manipulation detected by afm and fluorescence

Scientific background

Chemistry is often regarded as the science of recombination at the atomic level to form new molecules comprising either single atoms or simple atomic clusters linked via covalent bonds. The tools to obtain images of, or intervene in, such chemical processes at the level of individual atoms, are now becoming available to analyse and manipulate nanoscale structures in which molecules are linked by non covalent bonds.

The main breakthrough that has made this possible is the development and combination of new microscopy techniques that enable structures and processes to be resolved down to the molecular level. The principal development here has been the scanning probe and near field techniques, which enable surface structures to be resolved down to sub-nm resolution. The scanning probe approach involves locating a probe fitted with a tiny tip the diameter of a few nanometer to a single atom just above the surface to be scanned. In the case of scanning tunnelling microscopy as the tip approaches the surface, an electric current is induced in it by the quantum tunnelling effect that enables an electric potential barrier to be overcome at very small dimensions. The actual movement of the probe as it is positioned over different parts of the surface then enables an image to be constructed.

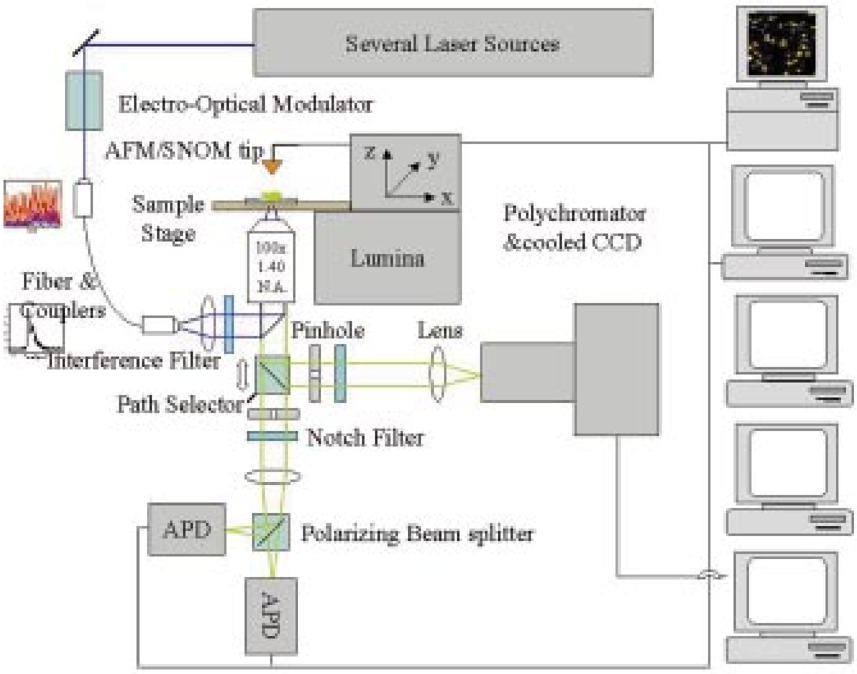
There have also been significant developments in optical microscopy, with near field and fluorescence techniques enabling organised molecular structures to be studied at surfaces.

Equally important are developments that enable molecular structures to be manipulated and assembled. One technique, which is being developed within the programme, is the use of laser beams to trap small structured systems so that they can then be imaged and manipulated.

Then for synthesising molecular structures, a variety of self-assembling techniques are employed, including H-bonding, and co-ordination chemistry.

H-bonding involves creating organic assemblies by exploiting the ability of hydrogen atoms to form non-covalent bonds with electronegative atoms, often nitrogen or oxygen.

Set up used for manipulation



Although the individual bonds are weak, stable structures can result when the bases are stacked in such a way that those adjacent bonds reinforce each other. Indeed the DNA double helix relies on such H-bonding for its stability. New ways of building structures have also been developed using organometallic intermediates.

Another important field of research concerns control of the shape of structures and the motions of molecules within them by use of externally applied forces such as irradiation or electric fields.

Aims and objectives

SMARTON has been split into the three branches of organic, inorganic and polymers, to strive for the ultimate goal of designing nanoscale systems that can be assembled in a controlled way with specific properties. Teams from different countries are making independent but co-ordinated contributions in one or more of the three branches. Dutch research groups for example are contributing in all three areas aiming to:

1 ▪ Synthesise dendritic structures (i.e. skeletal molecular structures that can be used to build crystalline materials) by covalent bonding or self assembly.

2 ▪ Development of molecular based switches that could contain information and be addressed by either light or focused local electric fields.

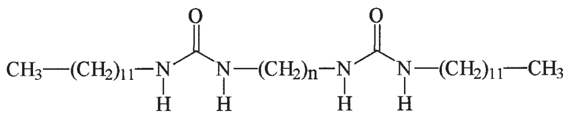
3 ▪ Construction of nanostructures by self assembly of molecular compounds via H-bonding or coordination chemistry (*see Scientific background*).

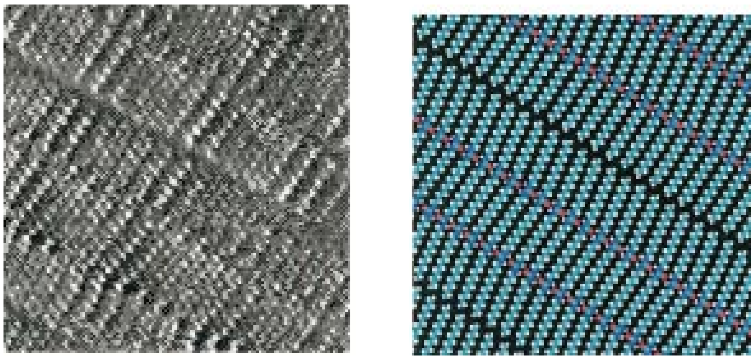
The eventual storage of information at the molecular level is of particular interest given the demand for ever smaller memory components in computers and electronic systems. In Holland a group at Groningen will work on molecules that can represent zeroes and ones by alternating between two states of helicity. One state is switched to the other by irradiating the molecule with polarised light.

The Max-Planck-Institute for Polymer Research is focusing particularly on the design, synthesis and processing of polymers. Both spectroscopic and non-spectroscopic methods are being used to examine the structure of polymers. Then the group will be applying its expertise at assembling polymers in a controlled way. There is special emphasis on tailoring molecular structures by controlling the stiffness of polymer chains, the directions of hydrogen bonding, and the packing of interdigitating alkyl chains (i.e. chains that interlock with each other).

A French group is focusing on molecular systems that can be controlled from the outside, with particular emphasis on electromechanical molecular engines. These exploit reversible changes between two bonding states of a compound where there is significant movement within the structure. By controlling the switching between the states, this movement can be harnessed for a molecular motor. The group has been studying various topologically novel systems such as catenanes (interlocking ring systems) for some years. Significant motions can be generated if a ring can be made to glide along a chain to which it is attached.

This group and other partners are now making new compounds and testing their ability to undergo the desired large geometrical rearrangements in solution. They are using probing techniques to assess the movements at nanometer scales after immobilising the compounds on a mica or graphite surface to avoid background motion.

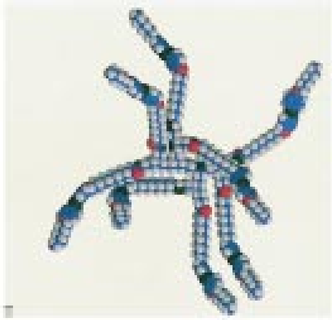




Scanning tunnelling image of a bisurea deritative

They are also interested in systems with two or more stable forms that can be switched upon application of light or electrons. They are studying the assembly of different chromophores in nanoscale structures via either covalent bonds or weak interactions. Attempts have been made to understand the role played by driving force, distance and orientation in the assembly, but there have been various drawbacks such as the shortage of available solvents. However the problems can be avoided by attaching the molecules on a surface such as mica or graphite. It so happens that photochromic or electroactive structures that possess two or more stable forms make good candidates for such studies, and this leads to the potential for storing information.

Laser trapping of dendrimers



Transmission image of trapped dendrimers

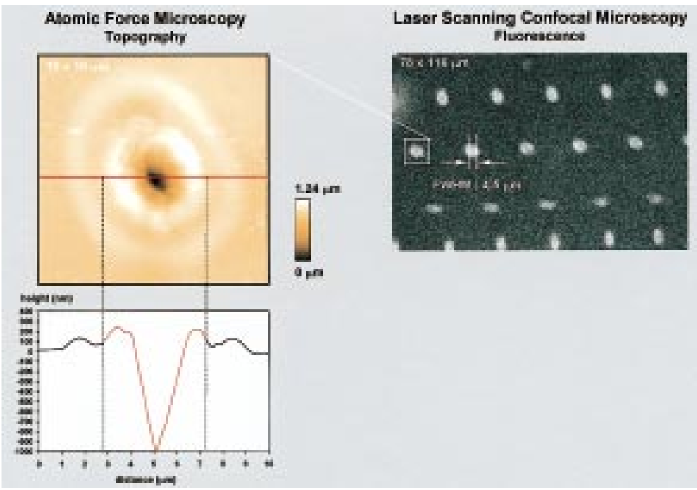
Fluorescence image of trapped dendrimers

The British partners are interested in the use of molecular recognition to generate new catalytic receptors and sensors that can be used to build new structures. A major focus here is the development of new structural tools that are needed to observe and analyse the large arrays this group is working on. The group has been using DNA as a molecular scaffold to organise proteins, lipids and oligosaccharides, and the resulting arrays are too large for the structural techniques used for conventional molecules.

The Belgian consortium is developing techniques that increase the spatial and time resolution with which structures can be studied. The group aims to facilitate spectroscopy of single particles, polymers and nanoscale entities using scanning probe methods coupled with photochemical transformation.

The ESF programme

IR-laser modified polymer film surface analysis using AFM and confocal microscopy



The five year programme is built around the individual contributions of the partners outlined under *Aims and objectives*, fostering increased collaboration and cross fertilisation between them. All participants have already secured funding within their respective countries for at least parts of their project, and the ESF programme is concentrating on pooling human and instrumental resources more efficiently, and encouraging faster and smoother exchange of materials and expertise. For this reason the ESF budget is being spent mainly on individual short scientific visits within the existing network infrastructure. Short fellowships will be given to young scientists to facilitate the integration of some of the existing programmes as agreed by the relevant research directors.

There will be three workshops, held every two years with limited attendance, to discuss topics of common interest to the network as a whole. Then in the two years when the general workshop is not being held, there will be meetings of specialised workgroups covering more restricted specialised topics.

There will also be meetings of the steering committee every six months to determine the content of workgroups and oversee the publication of joint research involving two or more of the participants.

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SMARTON Steering Committee

Professor Frans C. De Schryver
Department of Chemistry
KU Leuven
Celestijnenlaan 200 F
3001 Heverlee
Belgium
Tel: +32 16 327405
Fax: +32 16 327989
Email:frans.deschryver@chem.kuleuven.ac.be

Professor Jan Becher
Kemisk Institut
Odense University
Campusvej 55
5230 Odense
Denmark
Tel: +45 66 158600 ext. 2554
Fax: +45 66 158780
Email: JBE@chem.ou.dk

Professor Jean-Luc Brédas
Université de Mons
Service de Chimie des Matériaux
Nouveaux
Place du Parc 20
7000 Mons
Belgium
Tel: +32 065 37 33 56
or +32 065 37 33 62
Fax: +32 065 37 30 54
Email: jeanluc@averell.umh.ac.be

Professor Klaus Müllen
Max-Planck-Institut für
Polymerforschung
Ackermannweg 10
55021 Mainz
Germany
Tel: +49 613 379150/151
Fax: +49 613 1379350
Email: muellen@mpip_mainz.mpg.de

Professor R.J.M. Nolte
Department of Organic Chemistry
NSR Center
Toernooiveld 1
6525 ED
Netherlands
Tel: +31 (0) 24 3652143
Fax: +31 (0) 24 3652929
Email: tijdink@sci.kun.nl

Professor Jeremy K.M. Sanders
University Chemical Laboratory
Lensfield Road
Cambridge CB2 1EW
United Kingdom
Tel: +44 (0) 1223 336 411
Fax: +44 (0) 1223 336017
Email: jkms@cam.ac.uk

Professor Franz Stelzer
Institut für Chemische Technologie
Organischer Stoffe der
Universität Graz (ICTOS)
Stremayrgasse 16
8010 Graz
Austria
Tel: +43 316 873 8458
Fax: +43 316 815886
Email: stelzer@ictos.tu-graz.ac.at

Member from France to be appointed in 1999.

Dr. Hans U. Karow
ESF Senior Scientific Secretary

Mrs. Catherine Werner
ESF Programme Administrator

European Science Foundation
1 quai Lezay-Marnésia
67080 Strasbourg Cedex
France
WWW Home Page:
http://www.esf.org
Tel: +33 (0)3 88 76 71 28
Fax: +33 (0)3 88 37 05 32
Email: cwerner@esf.org

For the latest information on this programme consult the SMARTON home page (http://www.esf.org/pp/SMARTONa.htm)

Cover picture:
Set up used for manipulation
All pictures courtesy of Frans C. De Schryver

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