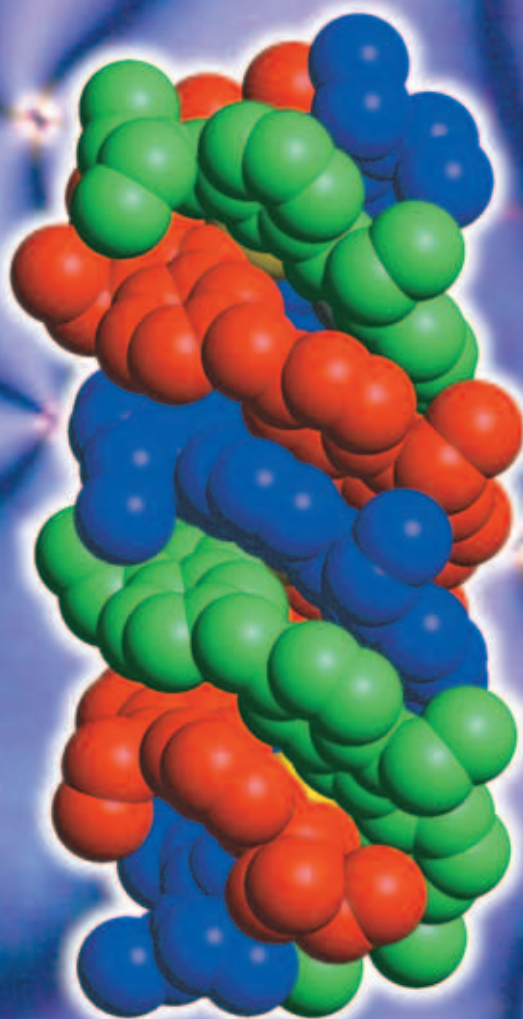


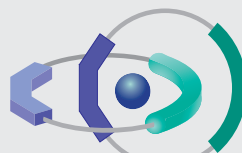
Special issue of Vision  
(September 2002)

# NRP

# “Supramolecular Functional Materials”



National Research Programme



Supramolecular Functional Materials

 *vision*

Science and Innovation Made in Switzerland



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## Foreword



### Dear Reader

A prerequisite for the development of new materials is solidly based fundamental research. However, the path from research results to the launching of a marketable product is often fraught with obstacles. The Swiss National Research Programme "Supramolecular Functional Materials", supported by the Swiss National Science Foundation, seeks to remove some of these obstacles by grouping a series of projects firmly rooted in fundamental research with the aim of reinforcing their potential for application. Complex supramolecular structures that

lead directly from the molecular dimension into the nanoscopic world can be built by means of targeted chemical synthesis; these structures may function as molecular machines, as detectors or transport systems and are themselves often inspired by biomolecules. In this special issue of *Vision* the different projects are presented highlighting the relationship between the projects and physics, biology and engineering; the content and thrust of this research is presented in a showcase to commerce, industry and the general public. Readers are invited to visit the participating chemistry laboratories, to experience the fascination of research and to conjecture on the potential for future applications for supramolecular chemistry.

Andreas Ludi, President of the Steering Committee of NRP 47 ■

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# Supramolecular functional materials

The National Research Programme (NRP) on “Supramolecular Functional Materials” was approved by the Swiss Federal Council within the framework of the eighth NRP series. Those in charge tried to find a title for the project which was comprehensible, factually correct and appropriate. However, it was difficult to be fair to both the specific community of specialists and to the interested public.

DR. MARCEL MAYOR\*, SCIENTIFIC ADJUNCT TO THE STEERING COMMITTEE OF NRP 47

Of the three words “supramolecular functional materials,” the first is certainly the least comprehensible to the general public. Something may be understood under the term materials as can the fact that these may have certain functions. For example, the material from which a raincoat is made has, preferably, the function of being “waterproof”. The material is, however, certainly not “supramolecular” like the new materials in question. The term “supramolecular” specifically describes the materials and functions we are dealing with. This is therefore the core of the title, the word which is able to explain the contents of the programme most suitably.

## Conventional molecules adhere strongly...

Close examination of the term “supramolecular” begins in conventional chemistry, which deals with the constitution and properties of molecules. Molecules consist of various atoms bound to each other by covalent bonds according to predetermined

laws. Covalent means that two neighbouring atoms share a certain number of electrons which hold the atoms together. In chemical reactions, two molecules react with one another by breaking existing covalent bonds to create new covalent bonds. At least one new molecule is created in the process, which once again consists of different atoms covalently bound to each other.



## ...supermolecules only adhere weakly

The components involved in supramolecular chemistry are also molecules. These fit together into very large structures, so-called supramolecular superstructures or supermolecules. Unlike conventional chemistry, these molecules do not enter into any new covalent bonds, but are held together

by relatively weak attractive forces which may differ in nature. For example, regions of neighbouring molecules with opposite partial charges attract each other. This is called electrostatic interaction. Or an electron-rich functional group of a molecule may bind itself to the hydrogen atom of one of the functional groups of the neighbouring molecule resulting in so-called hydrogen bonding. In most cases stable bonds may be preferred. However, certain essential concepts may only be achieved with weak, reversible bonds. These concepts are specifically put to use in supramolecular chemistry. “Molecular recognition” is one of these concepts.

### \* Marcel Mayor

Born in Zurich in 1965; studied chemistry at Berne University, where he completed his Ph.D. with work on supramolecular chemistry. During a subsequent postdoc stay at Strasbourg University, he became acquainted with Professor Jean-Marie Lehn, with whom he collaborated in the following years. After a stay at the Collège de France, he is now involved in setting up a new supramolecular working group at the Karlsruhe Research Centre's Institute for Nanotechnology, where he is conducting research in the field of molecular electronics. He is involved in NRP 47 as the Scientific Adjunct to the Steering Committee.

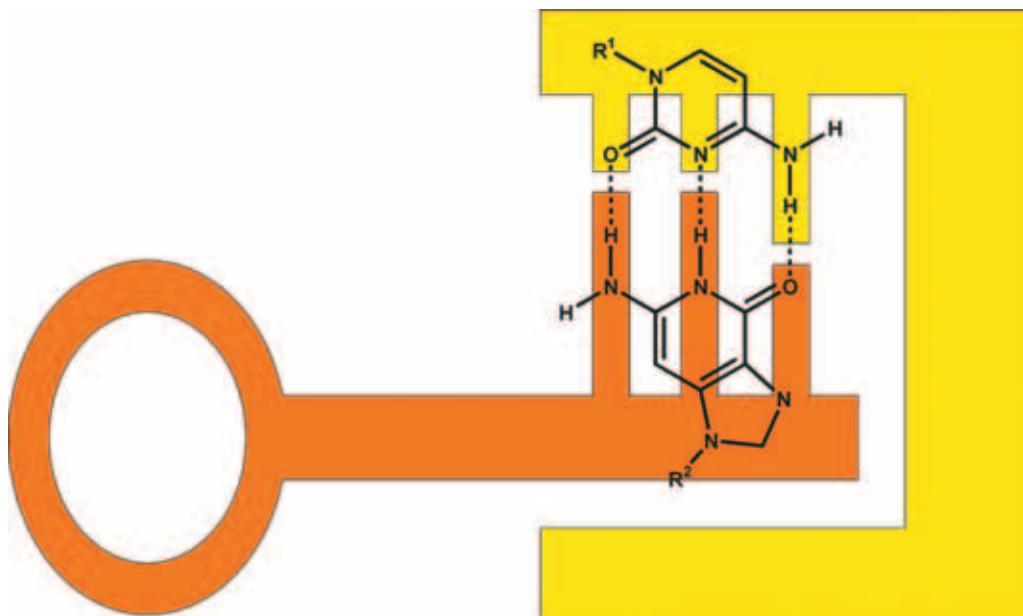


Figure 1:  
Two molecules,  
which fit  
together like a  
key in a lock,  
held together  
by hydrogen  
bondings.

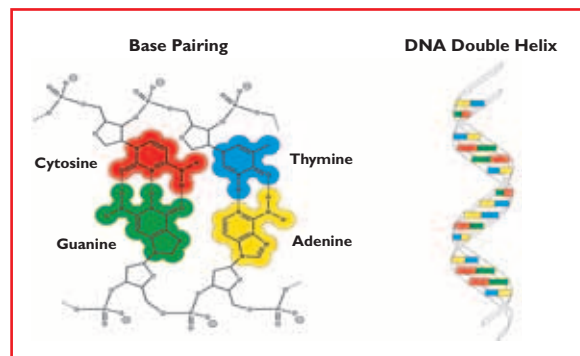
### Like a lock and a key

Molecules each have a distinct shape, size and functional groups. These properties are characteristic to molecules of a specific chemical composition. In order for two molecules to form a supramolecular superstructure, they must fit together externally, like a lock and a key (Figure 1). This was first observed by Emil Fischer, a Chemistry Nobel Prize laureate, more than a hundred years ago.

A further principle of supramolecular chemistry, called “selectivity”, also depends directly on this characteristic. Just as many keys may be tested in a certain lock until the proper one is found, a molecule may also try out different binding partners until it binds to the one which suits it best. The significance of this fact becomes clear if we bear in mind that the human genotype is stored, transferred, read and transformed by pairs of molecules which are held together by hydrogen bondings (Figure 2).

Molecules which are able to assemble spontaneously to form larger structures are interesting components for materials – we might liken these molecules to a kind of Lego brick which is able to assemble itself accurately and which knows exactly where it belongs in an architectural plan. The supramolecular construction plan is already stored in its components, the individual molecules.

Figure 2:  
Hydrogen bondings  
lead to the formation  
of base pairs which  
keep two DNA  
molecules together  
in a double strand.  
Right: The supra-  
molecular super-  
structure of two  
double-stranded  
DNA molecules is  
helical.



### Functions possible only in a structure

Some molecules have very distinctive physical properties. For example, they may absorb light or electrons and in the process change colour or shape. These functions may be taken into account in the construction programme. Thus, various interdependent functions may be concentrated together in a larger object. The object itself may be able to carry out complicated functions which the individual components would not be able to do on their own. Even the weak binding forces in these objects are an advantage. If individual components are damaged, the damaged component is replaced automatically by a new one which continues to function properly as it fits better into the construction plan. This automatic “healing” effect is only one example of the fascinating benefits anticipated from the use of “supramolecular functional materials”. ■

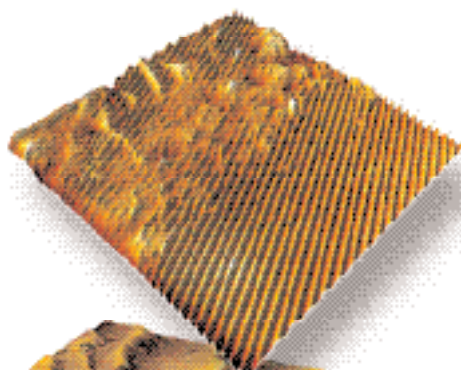
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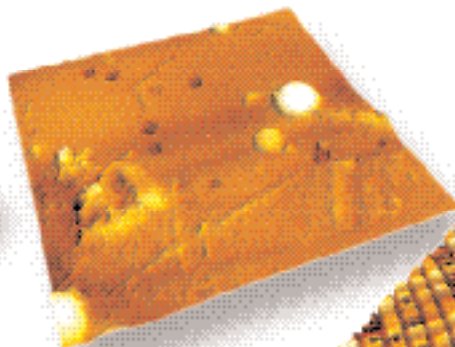
# Nanometer resolution for Surface inspection

smart SPM solutions

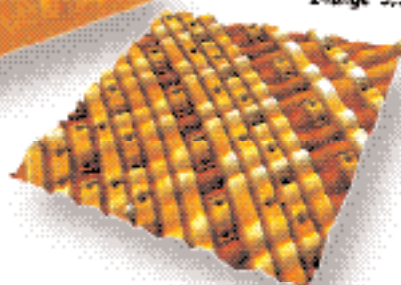
Injection molded polycarbonate with defects  
scan size 50  $\mu\text{m}$  z-range 200 nm



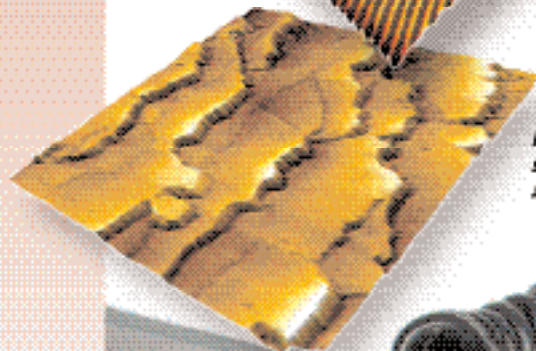
Plastic coating with defects  
scan size 80  $\mu\text{m}$  z-range 1,2  $\mu\text{m}$



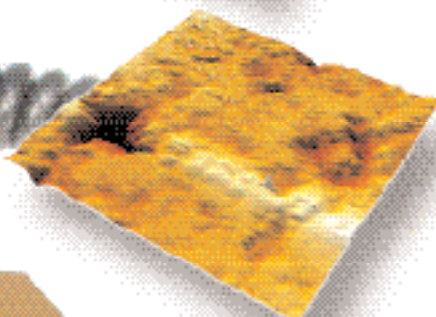
Microprocessor  
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z-range 3,5  $\mu\text{m}$



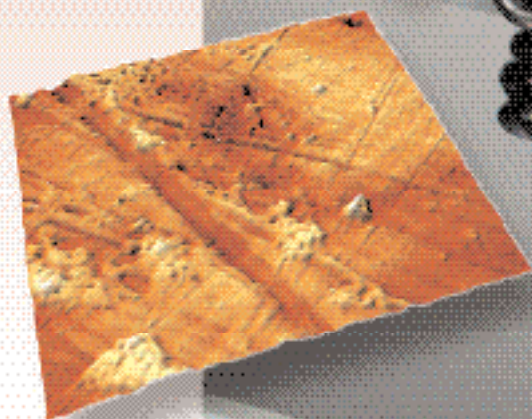
Human hair  
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z-range 2,5  $\mu\text{m}$



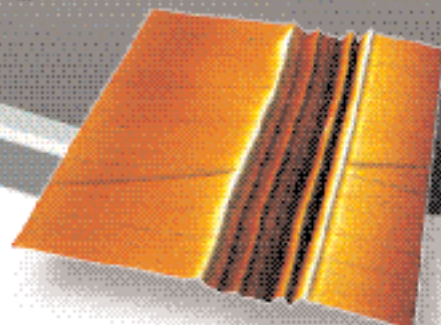
Grain analysis: sintered ceramics  
scan size 80  $\mu\text{m}$  z-range 11  $\mu\text{m}$



Polish tracks in metal  
scan size 12  $\mu\text{m}$   
z-range 300 nm



Stylus track  
scan size 85  $\mu\text{m}$  z-range 450 nm



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# Academic research and industry are complementary



Supramolecular chemistry, a matter of great interest to Ciba Specialty Chemicals, although applications still lie in the distant future.

**“Complementarity is essential in the collaboration between academic institutions and industry,” says Werner Rutsch, Manager of the Corporate Technology Office of Ciba Specialty Chemicals. “Each is capable of something the other is not – in co-operation a good solution is found faster.”**

Establishing early contact with industry is important, emphasises Rutsch. Thus, the practical requirements of industry may be taken into account at an early point in time. In his experience, it is frequently too late when the finished product already exists. There is, too, a high probability that the product is not optimally adapted to client requirements. However, Ciba does not wait for academic researchers to approach the company; it scouts current technology and takes action as soon as something interesting is found externally.

## Positive collaboration

The company today collaborates with more than 60 universities and academic institutions in 12 countries. This

## Who owns the patents?

The question of intellectual property or the right to patents is usually regulated by contract. In the past, these were frequently made with professors. Today, they are increasingly handled by technology transfer offices. If the parties' views on the commercial value of a patent or a discovery differ, they have to seek a fair compromise which takes account of the risks involved in financial participation in a project as well as the inventive contribution of the researchers. Financial compensation is mostly obtained through licence fees.

mainly involves counselling and advice agreements with professors and co-operations within which projects are carried out externally. Furthermore, eight Ciba R&D collaborators have lectureships at Swiss universities. “Our experience with academic contacts is very positive,” states Rutsch. Actual stimulus for new developments may originate from basic research, with industry taking on the role of transferring the technology into a commercial product. Conversely, the academic institution may investigate a phenomenon encountered by industry.

## Long-term collaboration

Industrial research today is under pressure to meet deadlines and to achieve results, which frequently leads to short-term research objectives being set. There is a great risk that this pressure will also be transferred to research in the universities. Rutsch is aware of this problem: “Universities have long-

term responsibilities with regard to education and basic research. Accordingly, any collaboration must also be long term.”

## Interest in supramolecular functional materials

Developments in the field of supramolecular functional materials are of great interest to Ciba. “We expect new opportunities to open up for us in this field and in that of nanoscience,” explains Rutsch. He sees practical possibilities in high-tech applications like storage of information, but also in traditional fields such as the protection of surfaces. The necessary expertise is available in-house: Chemistry Nobel Prize Winner Prof. Jean-Marie Lehn, an established expert in the field of “supramolecular chemistry”, as he calls it, is a member of Ciba's board of directors.

Ciba envisages practical application of supramolecular chemistry in its branch of industry only in the distant future. However, in the field of nanoscience, “We are very interested in nanoparticles. First developments in this field are already underway in our laboratory. Moreover, we are tracking progress at an international level in order not to miss any pioneering developments,” says Rutsch. ■

# The supramolecular construction site will have a crane

In the organic chemistry laboratory of the Federal Institute of Technology in Zurich, Professor François Diederich's team are developing molecular receptors. This project is in the newly emerging field of manipulation on a nanoscopic scale. This is currently an area of fundamental research for which industry has already expressed an interest.

“In the medium term, we are hoping to build a molecular crane,” explains Diederich. “Like its macroscopic counterpart, this crane must be able to pick up an object, transport it, and then put it down in defined place and at a defined time. The object in question is a molecule and the crane should thus enable us to obtain functional supramolecular assemblies.”

“Interdisciplinarity not withstanding, I must continue to be a specialist in a particular field.”



## François Diederich

Born in 1952 in Ettelbruck in Luxembourg. After taking a degree in chemistry, he obtained a science doctorate in 1979 from the University of Heidelberg for a thesis on organic chemistry. He then took a post-doctoral course at the University of California in Los Angeles. On his return to Heidelberg, he went into the field of supramolecular chemistry when writing his habilitation thesis on the molecular recognition of synthetic cyclophane receptors that he completed in 1985. Since 1992, he has been Professor of Organic Chemistry in the Federal Institute of Technology in Zurich.

Fields of application: Supramolecular construction, bioanalytics.

## Molecular affinities

It is already possible to manipulate atoms or molecules individually. That can be done by any scanning probe microscopy technique. “The drawback with this technique is that it is destructive,” the researcher explains. “In the case of the scanning tunnel microscope, an electrical pulse is necessary to snatch a molecule from its original site and release it where you want it after moving it.”

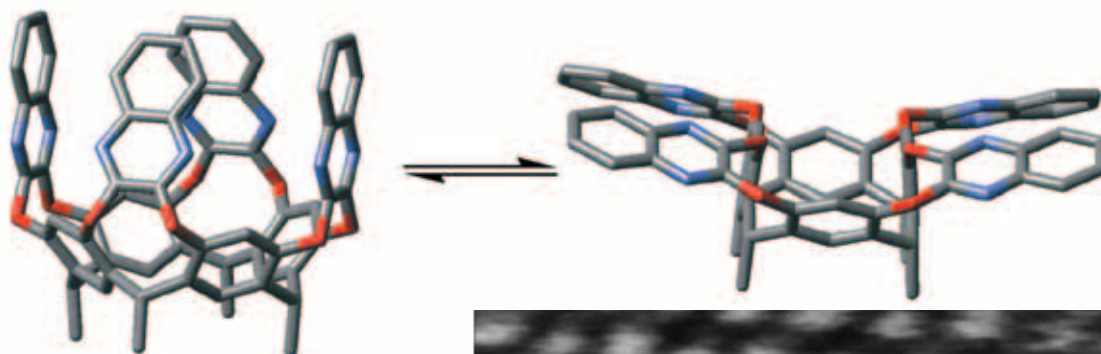
The Zurich approach prefers not to use force to displace a molecule; it simply wants to use “a molecule’s natural affinity for another molecule.” This phenomenon is called molecular recognition. “This concept lies at the heart of many biological processes. It describes the property of a molecule acting as receptor to recognize and to retain another molecule.”

## Dynamic receptors

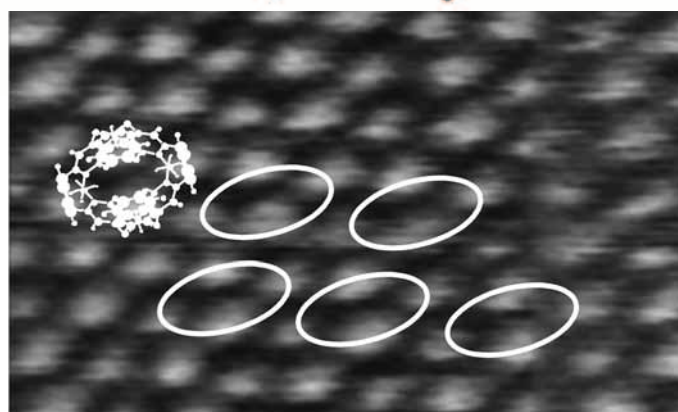
The receptors being studied in Zurich were brought to light by the team headed by Professor Donald J. Cram, who was one of the three chemists who shared the Nobel Prize for Chemistry in 1987 and who died in July 2001. These are what are known as dynamic receptors that can take two different forms the scientists call “conformations.” A vessel-shaped conformation enables a receptor to capture a specific molecule by molecular recognition, while an open conformation permits its release.

The structures of the two conformations are known. Prior to the work done by the group in Zurich, the only stimulus enabling transition from one conformation to the other was a change of temperature. “Not a very





The two conformations of the receptor allow the device to pick up a molecule, transport it, and then release it. The receptors can be attached to a surface.



6 nm

**Module I:**  
Information storage, molecular switches and wires

practical technique," Diederich concedes. "Following a suggestion by the President of the Programme Steering Committee, Professor Andreas Ludi, we discovered another possibility: changing the pH."

### Important work of synthesis

One of the main aspects of the Zurich project is the use of organic synthesis to modify different areas of the receptors to make them more effective. A modification of the edge, for example, allows greater selectivity in relation to certain molecules. The addition of functional groups called "legs" enables the receptors to attach themselves to solid surfaces. "We were able recently, in collaboration with IBM, to view a layer of receptors on a gold surface," Diederich commented. Scale is another fundamental concept. The researchers in Zurich no longer want to work with a sample of molecules, but with a single molecule. "For almost twenty years now, chemists have been applying the principle of molecular recognition to molecules in solution. Today, we have the capability

to work on a single molecule." There are various techniques that allow observation on this scale, the main ones being fluorescence spectroscopy and scanning probe microscopy.

### Indispensable collaboration

"This research is highly interdisciplinary," stresses Diederich. "But you can't do everything. I want to stay at the peak in my fields of expertise, the design and synthesis of complex organic molecules capable of expressing a desired property or function. For the other aspects, mainly display methods, we have to make collaboration arrangements, like those that we have with IBM, which is a world leader in the field of scanning probe microscopy and which also provides a remarkable environment at the human level." ■

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# Films for communications

**Modern technologies in the field of telecommunications increasingly resort to the use of light as a medium for processing or transmitting information. Professor Peter Günter, director of the Non-linear Optics Laboratory at the Swiss Federal Institute of Technology Zurich (ETHZ), hopes to participate in this trend by developing supramolecular films that can be used to alter or modulate optical waves.**

“We are trying to develop supramolecular organic materials capable of modulating a light signal, for example by changing the propagation velocity or even the intensity of the wave,” explains Peter Günter. “If these changes are made according to a specific code they can be used to transmit a large amount of information via an optical wave in a short period of time.”

To serve this purpose the materials being developed in Zurich have to have either electro-optical or non-linear optical properties. “In the first type of material, the propagation velocity of a wave may be changed by an electric field. In the second type, a single optical ray is sufficient to change the properties of another optical ray. Our research covers both these directions.”

Field of application:  
Optical telecommunications.

## Ordered molecules

Many organic molecules that have properties suitable for use as bases for materials with nonlinear optical properties have already been identified today. Among these are some new so-called polar molecules which have been developed in recent years at the ETHZ; these would be suitable for use in applications in the field of opto-electronics if it was possible to arrange them into good films. “The initial molecules already have very interesting properties,” continues the researcher. “For them to be useful at a macroscopic scale, the molecules need to be aligned parallel to each other within the material. Research into this molecular self-assembly process has been limited and it is therefore not controllable. First, we need to add a functional

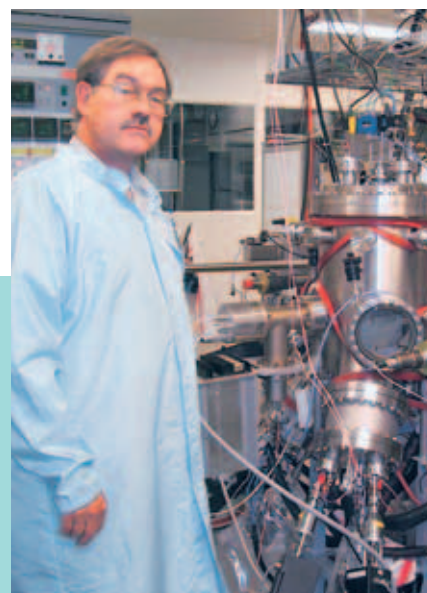
group to the initial molecule which allows it to recognise its neighbours and organize itself in relation to them.”

## Films versus crystals

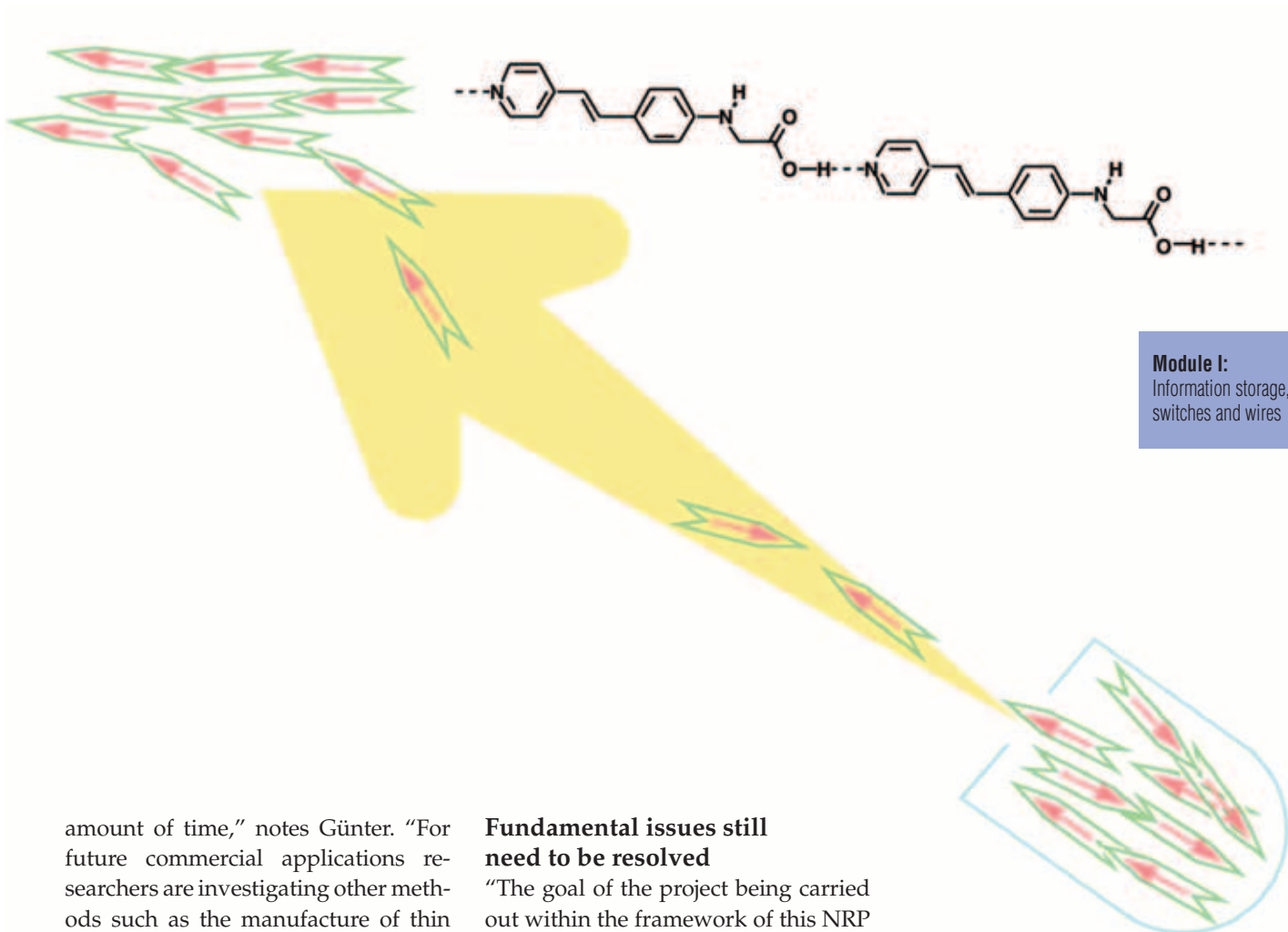
Crystalline arrangements with non-linear properties have already been identified. The Zurich group has to its credit synthesised an organic crystal with the greatest nonlinear optical effect in the world, the DAST crystal. “Unfortunately, preparation of the crystals requires a relatively large

## Peter Günter

Studied physics and mathematics at the ETH Zurich. In 1976, he obtained his Ph.D. for a thesis on the electro-optical and photo-refractive properties of  $\text{KNbO}_3$  crystals, for which he was awarded the ETHZ's silver medal. In 1982, he received the appointment as external lecturer in applied physics and in 1986 he was appointed Professor of Experimental Physics. Today, he is head of the Nonlinear Optics Laboratory where he is working on the development and application of new materials for information processing, telecommunications, and optical data storage.



“Supramolecular organic films may represent the ideal solution.”



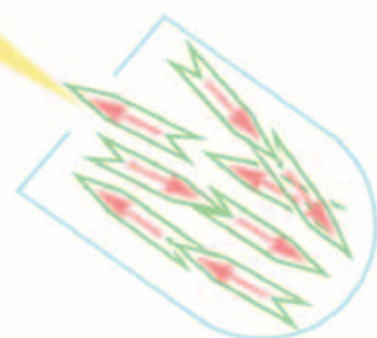
**Module I:**  
Information storage, molecular switches and wires

amount of time,” notes Günter. “For future commercial applications researchers are investigating other methods such as the manufacture of thin films with nonlinear optical properties. One method might be to deposit molecules on a substrate in order to obtain a supramolecular film.”

To obtain these films, the Zurich group had to develop a technique called Oblique Incidence Organic Molecular Beam Deposition. Using this technology, which requires equipment that fills the whole laboratory, molecules are first heated, then evaporated. Subsequently, they are bunched together into a molecular beam which is directed at a specific angle onto a surface where they assemble automatically. “We have already obtained our first films and carried out our first analyses. These results are very encouraging. However, the nonlinear properties evident are still too weak for future applications.”

### Fundamental issues still need to be resolved

“The goal of the project being carried out within the framework of this NRP is to fully understand and investigate the alignment of the molecules,” concludes Günter. “We already have the first results which indicate that alignment depends on the angle at which the molecules arrive on the substrate. There are still a number of fundamental issues which need to be resolved before thinking of applications. However, during this project we wish to attain sufficient understanding to enable us to lay the foundation for future applications in electro-optics and in nonlinear optics.” ■



Using the so-called Oblique Incidence Organic Molecular Beam Deposition technique molecules can be deposited on a surface to obtain ordered supramolecular films.

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# Long-lived metastable states

“The interaction between the molecules in the structure is critical.”



**Professor Andreas Hauser and his project partners are specifically preparing structures with long-lived metastable states. The optical or magnetic properties vary also with the states. This behaviour may be useful for applications like molecular switches as well as for data storage.**

If molecules are excited with light, they generally reemit the absorbed energy rapidly and in the best case, they begin to luminesce and return to their ground state (Figure 1). Professor Andreas Hauser is investigating structures which retain the excited state for a long time and make the energy absorbed available for subsequent actions or whose optical and magnetic properties change on a state transition. The spin-crossover compound based on iron(II), which basically meets the requirements for an optical storage

Field of application: Information storage and processing.

medium, is viewed as a classical model in this field of research, although it is not actually a supramolecular material.

Three researchers from three universities are collaborating closely in this field to attain common goals. Hauser is a physico-chemist interested in the photophysical properties of compounds which are being synthesised by his project partners. Professor Thomas Ward is the expert in synthesis chemistry with a solid background in organic chemistry and Professor Silvio Decurtins is engaged in coordination chemistry and magnetism of supermolecules. “At present our project is in the molecular synthesis phase,” states Hauser.

“We want to produce systems with long-lived metastable states as they result in interesting changes in properties.” This is the goal of the project as described by the trio of researchers. The components are coordination compounds in which a metal ion is surrounded mainly by organic molecules, so-called ligands. The researchers want to vary both the metal

(left to right)

## Thomas Ward

Studied chemistry in Fribourg (CH) and gained his Ph.D. at the ETH, Zurich. Post-doctoral stays at Cornell University and Lausanne University. Worked at Berne University until 1999, since 2000, professor at Neuchâtel University. In 2001, Swiss National Science Foundation Professorship for the promotion of science. Research topics: supramolecular catalysis.

## Andreas Hauser

Studied chemistry and gained a Ph.D. in Berne. Post-doctoral stays in Canberra, Australia and Mainz, Germany. From 1992 to 1996, engaged in the SNF's project Profile-2 in Berne. Since October 1996, Full Professor of Physical Chemistry at Geneva University.

Research topics: photophysical and photochemical properties of coordination compounds.

## Silvio Decurtins

Studied chemistry at Zurich University, Ph.D. at Berne University. Post-doctoral stays in the USA and in Germany. Spent 4 years in industrial research, including one year at the ETH, Zurich, and one year at Lancaster University (England). Since 1998, Professor at Berne University. Research topics: inorganic chemistry, supramolecular chemistry, molecular magnetism.

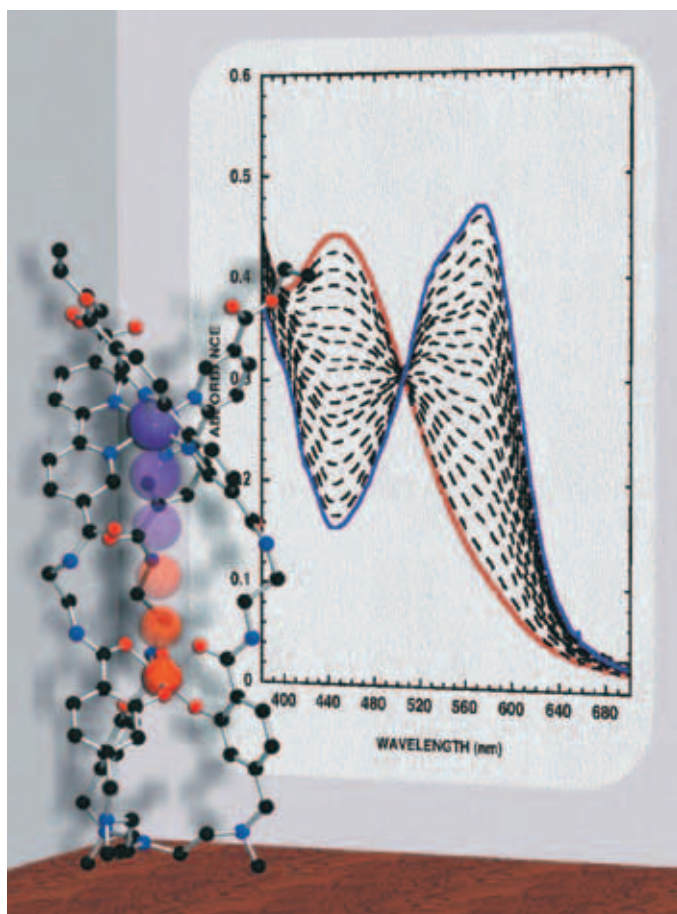


Figure 2:  
Structure with  
the properties  
of a molecular  
switch.

centres and the ligands, and combine them in supramolecular structures.

### A migrating metal centre

A good example is the triple helicate from Ward's laboratory (Figure 2): this is derived from an iron(II) ion (violet spheres) in an environment of three bipyridine-like ligands. Oxidation into an iron(III) ion, a harder ion, leads to migration of the metal centre into the lower end of the macromolecule, where it is surrounded by salicylamide ligands (red spheres). The corresponding light absorption spectrum changes dramatically. The blue line indicates iron(II), the red one iron(III). The process and the change of absorption are reversible, which means that this structure has the properties of a molecular switch.

### Electron transfer induced by excitation energy and light

If the complex components are combined to form a supramolecular structure, interactions occur between the molecules. "The interactions in the structure are critical," explains Hauser.

"An individual molecule may lose its particular physical properties or gain additional ones." The opinion of Decurtins: "This is exactly the goal that molecular engineering is seeking to attain in the field of supramolecular functional materials."

For this purpose, Ward is now synthesising molecular compounds, wherein, in an extension of the molecular switch concept, different co-ordination locations are occupied by different metal centres in different oxidation states. Decurtins is preparing compounds with metal centres which are coupled with each other in expanded lattices. Each metal centre with its ligand environment forms a chromophore unit, which when excited by light, is able to perform various functions depending upon the properties of the neighbouring centre. For example, the compound may assume the function of an electron donor or acceptor. Thus, it should be possible to achieve long-lived charge transfer states through photo-induced electron transfer enabling both storage of information and storage of energy.



Figure 1:  
Luminescence  
of a ruthenium  
complex.

**Module I:**  
Information storage, molecular  
switches and wires

However, the excitation energy may also be transmitted by energy transfer to the neighbouring unit; luminescence then terminates in the chromophore unit which was originally excited, and it is initiated in the neighbouring unit. A further important aspect, which is particularly taken into account in the molecular structures of Ward, is that these processes in the supramolecular structures can be steered. ■

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# Polar crystals

“Solid solutions are an excellent basis for designing materials in the technical world.”



## Jürg Hulliger

Studied chemistry at the ETH Zurich and gained his Ph.D. in 1984 at Zurich University. Post-doctoral studies at Pennsylvania State University, USA. Worked as a scientific researcher and lecturer at the ETH and at Zurich University. Since 1993, Jürg Hulliger has been Professor for Chemistry and Crystal Growth at Berne University. He has held various guest professorships and sabbatical positions at the Max-Planck Institute for Solid State Research, Stuttgart. Research topics: materials science orientated chemistry, crystal growth and liquid phase epitaxy, solid state theory and physical properties.

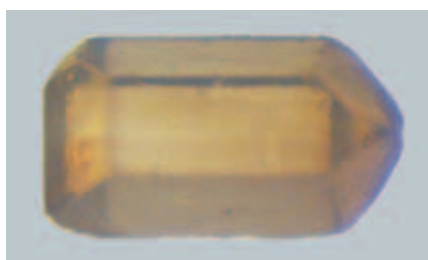
Professor Jürg Hulliger's research group at the University of Berne designs, crystallises and investigates polar molecular crystals. The group's interest is focussed on so-called solid solutions as well as on crystals with channel inclusions. A large field of high-tech applications for polar crystals is beginning to emerge ranging from sensor technology through information storage to frequency conversion.

Fields of application: Sensor technology, information storage, optical computers, frequency transformers or filters.

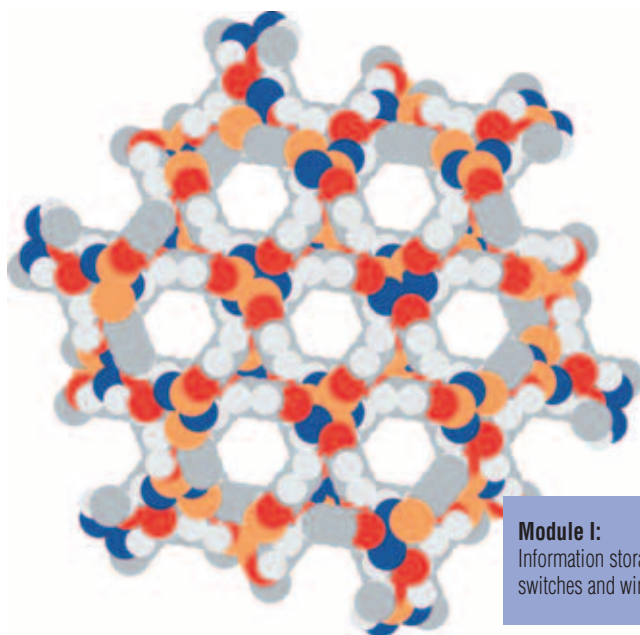
It's the dream of any materials' designer to be able to predict the properties of his materials. "We are concentrating our efforts on electrical polarity, because as a physical property, it is much easier to predetermine than for example the melting point of a substance or some other colligative properties," explains Hulliger. The goal of his project is to produce polar crystals made from several molecules systematically and to study them. A crystal's polarity is established by the combined polarity contributions from each individual molecule, the sum of which gives the total polarity. Statistical analysis of a databank of all known and investigated molecular crystals shows that only one fourth of the structures are polar. In all the other cases, molecules are arranged in the crystal so that no polarity results. "Our initial question is therefore: can a method be developed which always

leads to a polar crystal built out of polar molecules?," says Hulliger summarising the basic idea of his project. His approach comprises four steps

- Quantum mechanical estimation of the intermolecular interactions
- Estimation of the expected polarity with the help of a statistical theory on crystal growth and interaction energies
- Synthesis of the molecules and crystallisation
- Measurements of polarity using own methods.



Penetration of the zeolite crystal (left) by guest molecules which cause changes in colour at the end surfaces (centre). After completion of the process, the whole crystal is coloured. Right: Molecular structure of the crystals.



**Module I:**  
Information storage, molecular switches and wires

His studies are focussed on two types of material: so-called solid solutions and channel-type inclusion compounds.

### Solid solutions

“Solid solutions are an excellent basis for designing materials in the technical world,” explains the scientist. “This describes nothing other than a solid, in which certain locations in the structure are occupied by statistically distributed foreign atoms or molecules. Gold-silver alloys or a germanium-doped silicon crystal are exemplary solid solutions.” The Bernese research group has recently managed to crystallise polar molecular crystals which consist of non-polar and polar molecules with a quasi-identical structure. A solid solution in point of fact in which the build-up of polarity will be further investigated.

### Channel-type inclusion compounds

The crystals synthesised by Hulliger’s group consist of molecules – host molecules – which self-assemble to form channel-shaped voids where various guest molecules may be deposited. The Bernese researchers were able to conduct interesting experiments on such organic zeolites; in these the molecules in the channels were exchanged for a large number of other molecules (see illustration). For instance, stable radicals (molecules with one free electron) or molecules with 60 and 70 carbon atoms (C60, C70) were placed in the channels. In particular, they were able to show that the zeolite used absorbed gaseous iodine or iodine dissolved in water at a high rate. This observation is now the subject of a patent application, which some day may lead to the manufacture of filters for radioactive iodine (for the disposal of radioactive waste).

### A wide field of possible applications

“Many basic components in the high-tech world are polar: diodes, transistors, pressure sensors, oscillating quartzes in watches or frequency doubling crystals,” enumerates Hulliger. He can envisage many potential applications for the results of his research. He is open to collaboration with industry, and he is also successful. How-

ever, he considers that the priority function of academic research is the creation of intellectual products, for example theoretical models for the solution of problems. Although many promising results have been attained, Hulliger’s group is faced with new challenges in the next stage of the programme: he wants to synthesise more solid solutions and provide experimental evidence for the theories advanced concerning bipolar crystal growth. ■

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# Mechanically induced colour changes

## Beat A. Keller

Studied chemistry and biochemistry and gained his Ph.D. at Zurich University. Post-doctoral stays at Stanford University and at Zurich University. Worked for three years as a research chemist at EMPA. Since 1993, he has been group leader for Organic Interface Technology at EMPA. Lectureships: since 1994 at ETH Zurich and since 1999 at Buchs Technical College.



absorption of light. The structure of the polymer film may be influenced by an appropriate choice of starting material.

## Components for storage of information

Using diacetylenes as the starting material, the Dübendorf research group produces a thin film (Langmuir-Blodgett film), which is subsequently polymerised. In the next step, the film surface is structured with a special tool

“New impetus for information storage in polymers.”

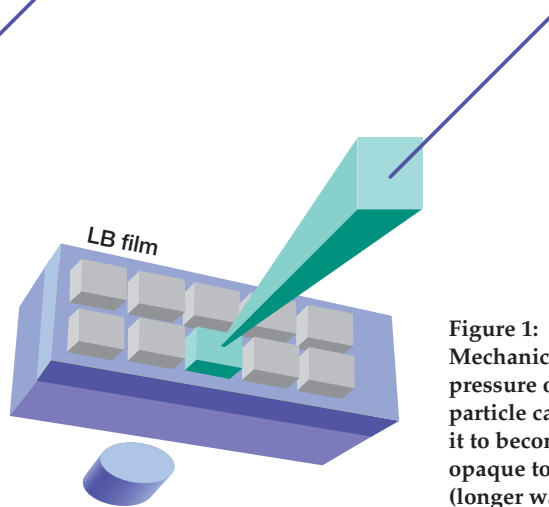
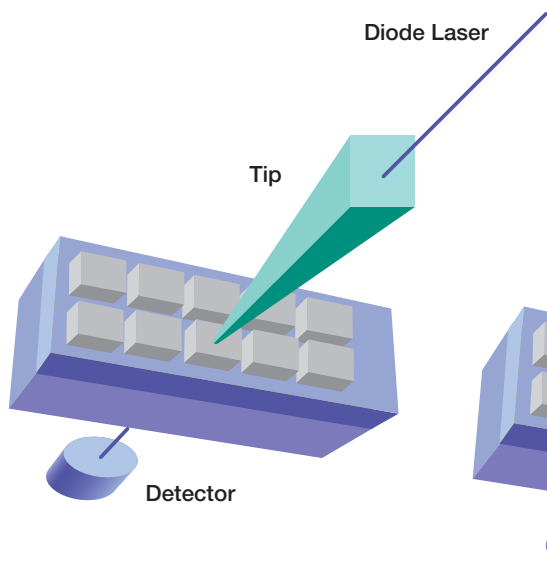
**At the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in Dübendorf Dr. Beat A. Keller’s research group produces polymers from molecules with multiple bonds. If the polymers are exposed to mechanical pressure, their light absorption qualities change. It may be possible to use this property in information storage applications.**

Starting point for the project was a scientific contribution which reported on polymer materials in which a change in colour could be induced by changing external conditions. The authors utilised this property to prepare a sensor for biological antibodies. “This led to the idea that this change in optical absorption could not only be used in a sensor but also quite generally as a medium to carry information,” explains Keller. The chromatic behaviour of these materials may not only be influenced by an antibody-antigen reaction, but also by other external influences, for example solvent effects, or heat or mechanical pressure. In the case of mechanical pressure this effect is called mechanochromism. The reason for this supramolecular property lies in distortions of conjugated double and triple bonds which are responsible for the

into tiny squares each with a side length of a few nanometres. Keller explains: “Each of these units contains the supramolecular property of the whole system. I want to be able to address each unit individually and to exert mechanical pressure on them with the tip of any scanning probe microscope, for example a near field optical microscope. This action offsets the absorption range and each small square becomes an information carrier medium in answer to the questions: Was any stress detected or not? Is it capable of letting laser light of a determined wavelength through or not?” (Figure 1). Keller expects new stimuli for the process of information storage in polymer materials from this quality.

Fields of application: Sensors, solar cells, display screens.



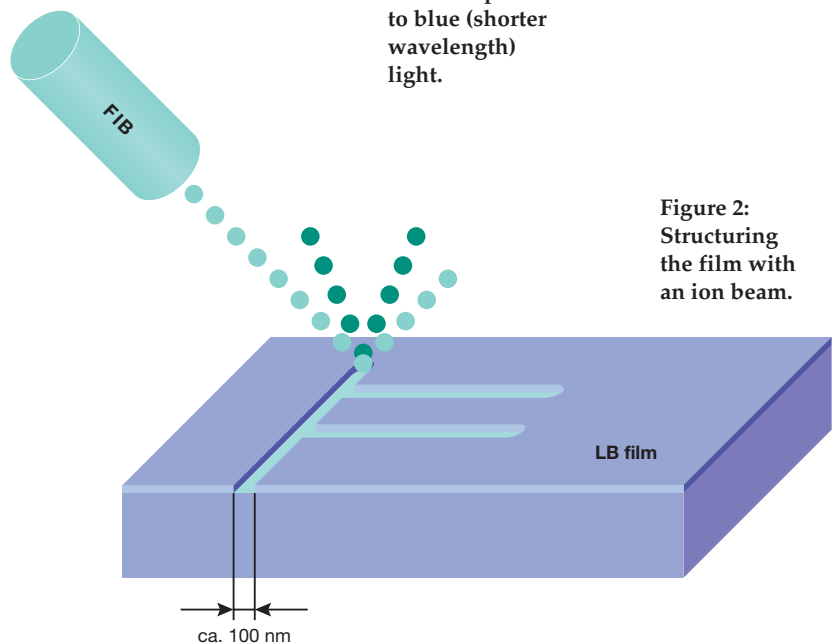


**Figure 1:** Mechanical pressure on the particle causes it to become opaque to red (longer wavelength) light and transparent to blue (shorter wavelength) light.

**Module I:**  
Information storage, molecular switches and wires

### Explanations are required

Several questions remain unanswered. How small may the squares be before they lose this supramolecular property? How can the film be structured? How much pressure is required to produce the change in colour? Is the change reversible? How fast is the process? These questions are directed to Keller's project partner, Prof. Wilfred van Gunsteren at ETH Zurich, who is seeking the answers using quantum chemical and molecular dynamic simulations. On the experimental side, today's most significant challenge is the homogeneous production of larger pieces of polymerised film and structuring it with an ion or electron beam (Figure 2). Finally, a system needs to be developed with which each individual square may be addressed.



**Figure 2:** Structuring the film with an ion beam.

### Sensors and switches

In addition to implementing the application for information storage, Keller envisages the construction of sensors with one or several receiver molecules as well as switches for microreactors. "I am trying to maintain contact with industry even though we are still working on many fundamentals," explains the Dübendorfer researcher, "and there also some international contacts." ■

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“Responsive nanocapsules”

# A molecular Trojan horse

At the Institute for Physical Chemistry of Basle University, researcher and lecturer Wolfgang Meier and his team have managed to synthesise tiny artificial hollow spheres inspired by nature. These nanocapsules, which have the capability of delivering, absorbing and protecting various substances in a specific manner, are bearers of hope notably in medicine where they could provide targeted delivery of drugs in the human body.

In chemistry or in pharmacology interest usually centres on contents, the active ingredient, rather than on the container, the medium. However, both concepts are fundamental, as Meier explains: “Assume a patient is affected by a genetic disease and is suffering from the lack of a specific enzyme. It is impossible to introduce this enzyme directly into his body. His immune system does not allow us to do this. On the other hand within a capsule, the enzyme is protected. And in the capsules which we are developing the enzyme remains effective.”

## Between 50 and 500 nanometres

The capsules are tiny hollow spheres, invisible to the naked eye: they usually vary in size from 50 to 500 nanometres in diameter. The walls are made from polymers. The main appeal of these

Fields of application: Medicine, pharmacology.

“We have demonstrated feasibility, let us now demonstrate utility.”

nanocapsules lies in the fact that the permeability of the walls may be changed easily. “A substance present inside the capsule can thus be released to order,” explains Meier.

These substances may be of different types – drugs, dyes... – opening up the potential for numerous applications.

## Artificial viruses...

Meier’s group makes use of two different strategies, both inspired from nature, to produce the nanocapsules. In the first approach, the Basle team tried to imitate a plant virus, the CCMV (Cowpea Chlorotic Mottle Virus). What is appealing in this model is the fact that the size of the protein envelope and its permeability change according to the acidity of the medium in which the virus is located. The virus envelope should be thought of as a net. When the envelope is folded upon itself – as occurs in the case of high acidity – the mesh of the net is tightened and the membrane becomes impermeable. Conversely, when the volume of the envelope expands – as in the case of low acidity – the mesh expands and a substance contained inside the capsule may then be released.



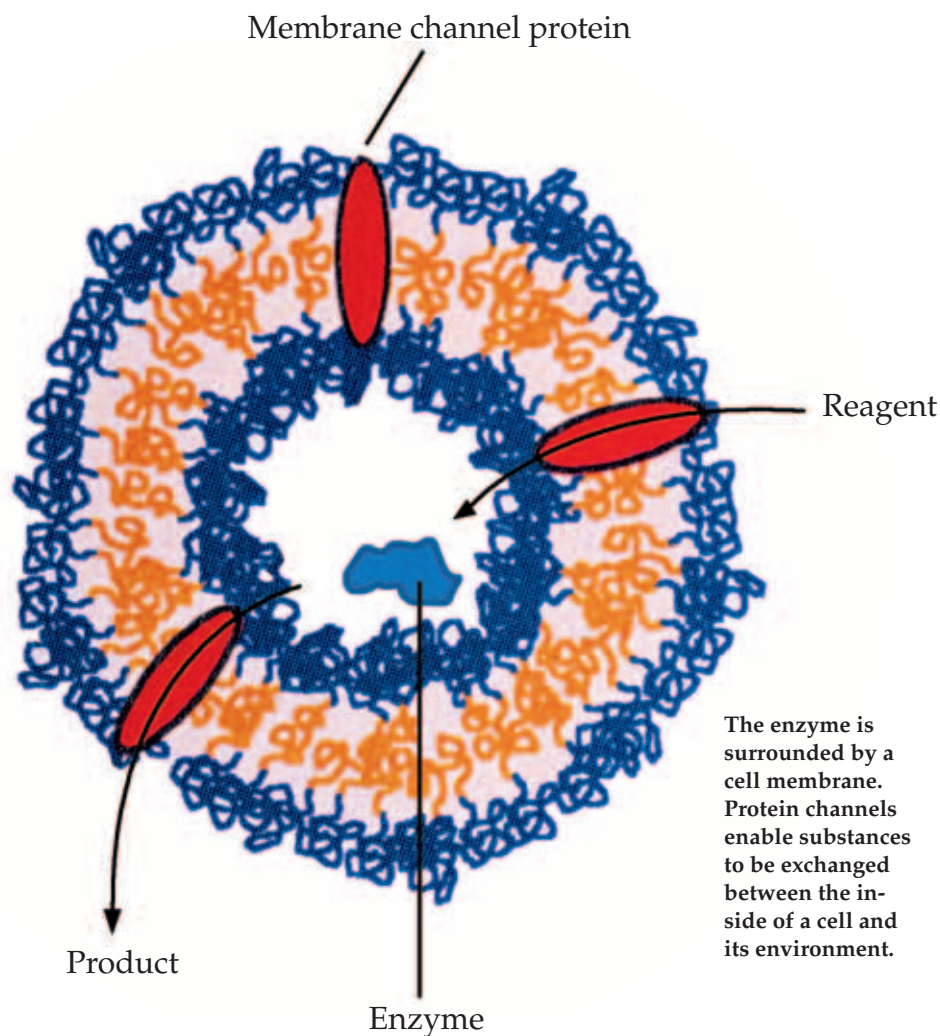
## Wolfgang Meier

Born in 1964 in Biberach, Germany. Studied chemistry at Freiburg-in-Breisgau University. In 1992, he also received his Ph.D. for thesis work relating to polymers which formed a liquid crystal phase. Since 1996, he has managed his own group and is able to conduct independent research at the Institute for Physical Chemistry of Basle University. His fields of interest are polymer chemistry and colloid chemistry.

Scientists have managed to isolate this natural envelope and encapsulate a substance inside it and observe how the surrounding conditions affect its release. “Technically, working with viruses is not easy,” explains Meier. “That’s why we are trying an artificial approach using polymers instead of proteins.”

## ...and artificial cells

For the second approach researchers were inspired by the biological cell. The cell is surrounded by a membrane transversed by protein channels which enable matter to be exchanged between the inside and the outside of the cell. Analogous to this natural arrangement, Meier’s group has synthesised artificial nanocapsules from polymers and placed natural protein channels on their surfaces. Depending on the



**Module I:**  
Information storage, molecular switches and wires

The enzyme is surrounded by a cell membrane. Protein channels enable substances to be exchanged between the inside of a cell and its environment.

type of channels selected, only certain specific substances may enter or leave the cell.

To test the efficiency of such a system, Meier's group encapsulated an enzyme capable of breaking down an antibiotic. The capsule was then immersed in a solution containing this antibiotic. The enzyme, which was too large to pass through the protein channel, remained confined in the capsule. The antibiotic, which was smaller, was able to pass through the channel and react with the enzyme; this was demonstrated by a reduction in the antibiotic concentration in the solution.

### Some time before they appear on the market

At the present stage of research, the Basle group has mastered synthesis of both of these types of capsule. "Both

methods were the subject of publications in professional journals," notes Meier. "The goal is now to think about the potential provided by such systems." The researcher already has contacts with companies in the chemical sector. "But it will still be some time before any product is marketed."

The situation of the Basle group is interesting. "We are the only ones who have such substances. Only last year we demonstrated the feasibility of encapsulating a natural protein in an artificial polymer envelope. Many colleagues thought this was impossible. Now we need to demonstrate the utility of our research." ■

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# New bricks for supramolecular construction

**For Reinhard Nesper, Professor of Inorganic Chemistry at the Swiss Federal Institute of Technology Zurich (ETHZ), the materials available at present are unsatisfactory. How does he expect to improve them? By setting up a nanoparticle library.**

“Although materials science has been a recognized field for a long time, I reckon that those materials available today are not optimised,” explains Nesper. “A great deal needs to be done at the nanoscopic level: at that scale, materials are often more or less the result of random grouping of various particles with different compositions and sizes. With better control, their properties might be optimised.”

To illustrate his intention, the researcher recalls a recent collaboration with the Paul Scherrer Institute. “The idea was to develop electric batteries which would perform better than those presently available. We synthesised new nanoparticles which could be used to construct the batteries and to improve them. After five years’ work, we had developed a material which is still the best in the world in its category.”

Field of application:  
Supramolecular construction.

## Stronger properties...

The goal of this project is not to develop a specific material, much less a battery. Nesper works on the assumption that these tiny particles may prove to be useful in many fields. “Apart from the new properties available due to their size, all those properties observed in present materials are also available at the nanoscale. However, at this level they are stronger.”

Starting from this assumption, the Zurich researchers are developing a nanoparticle library. Engineers can then select the material desired depending on the properties required in the same way as a tool can be chosen from a tool box or products from a do-it-yourself shop catalogue.

## ...by modifying the composition, the surface and the shape

“We wish to generate a library of anisotropic nanoparticles from transition metal oxides – whose properties change depending on the direction from which they are observed,” continues the researcher. These particles have astonishing properties which are the result of a number of parameters: some derive from their shape, generally tubes or wires; others from their composition, mainly transition metals; still others result from their nanoscopic dimensions.

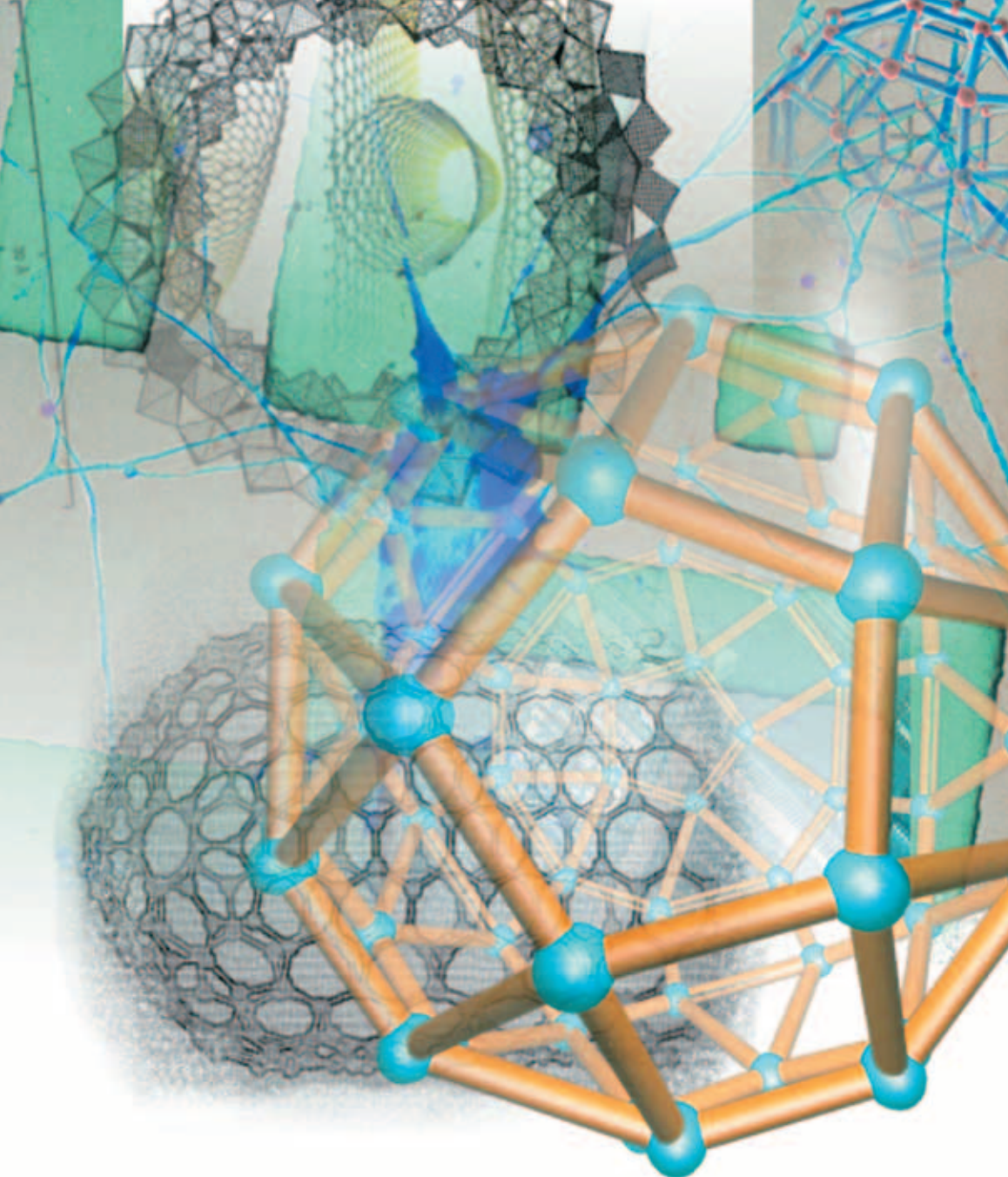
The treatment of the nanoparticle surface is another important part of this project. “This, for two reasons,” explains Nesper. “The change is signifi-



## Reinhard Nesper

Born in 1949 in Elze, Germany. He studied chemistry at Münster University. He completed his studies with a thesis on tin oxides which he carried out at the Max-Planck Institute in Stuttgart. In 1989, he habilitated at Stuttgart University. Since 1990, he has been Professor at the Laboratory for Inorganic Chemistry of the ETH Zurich. He introduced the field of solid state chemistry into this lab.

“Controlling materials at the nanoscale in order to enhance the functions.”



**Module I:**  
Information storage, molecular  
switches and wires

**Molecular  
representation  
of some  
nanoparticles.**

cant for subsequent combination of the particles with each other or for organising them on a surface. In addition, change may also impart a second function to the particle." The same nanoparticle may have its surface changed in different ways and thereafter display several functions.

### Secondary applications

"When we detect a particle with an interesting property – optical, magnetic or another – while we are setting up this library, we seek a collaboration with a partner to develop a product," explains Nesper. "Gradually, as the project advances, we are looking for

applications." However, he reminds us that this work is really fundamental research: "It is better to remain cautious when discussing potential applications because people quickly forget that we are only discussing a possibility and they expect products to be marketed within the year."

In general, industry is observing carefully what is going on in nanoscale research as the feeling is that present technologies will soon have reached their limit. "Companies are waiting on a new approach, new materials, new designs. The nanoparticles developed in Zurich might be their bricks," concludes Nesper. ■

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# Lanthanides and liquid crystals: a brilliant combination

In order to improve the luminosity of liquid crystal displays, the research team round Claude Piguet, professor at the Mineral Chemistry Department of Geneva University, is investigating what happens when certain types of chemical particles are integrated into liquid crystal materials. Although this project is more in the realm of fundamental research, it may soon be of interest to industrial circles.



## Claude Piguet

Born in Geneva in 1961. Studied chemistry at Geneva University. Again in Geneva, he obtained his Ph.D. in 1989 for a thesis in coordination chemistry. During this work, he became familiar with lanthanides. During a post-doctoral stay as a member of Prof. Jean-Marie Lehn's group at Strasbourg University, he was initiated into supramolecular chemistry. Subsequently he was appointed Assistant Professor (1995) and then Full Professor (1999) at Geneva University, where he is developing research into the supramolecular chemistry of lanthanides.

“This inductive approach is exciting.”

“Every time I looked at portable computer screens, I wondered why nothing could be seen if they are viewed at an angle greater than 10 or 15 degrees,” explains Piguet. “Once I understood that this was due to the fact that the low intensity light focussed in only one direction, I started to think how I could change this state of things.”

This is how the Geneva team came up with the idea of doping liquid crystal materials, which generally form the basis for these flat displays, with chemical substances which reemit light in all directions.

## Green, red, blue

“Three substances are required, each of which emits one colour, and when all three are combined white is attained a little like in television tubes,” continues Piguet. The chemical elements of the lanthanide series have these properties. Terbium (Tb) emits in

the green range and europium (Eu) emits in the red or blue range depending on its oxidation state. These substances are already employed in certain commercial products. But how can they be integrated into liquid crystals? That's the interesting question.

“This is difficult as lanthanides are rather bulky atoms, unlike the molecular units on which the liquid crystal material is based, which are generally flat and elongated. The natural tendency of lanthanides is to disorganise a liquid crystal state.”

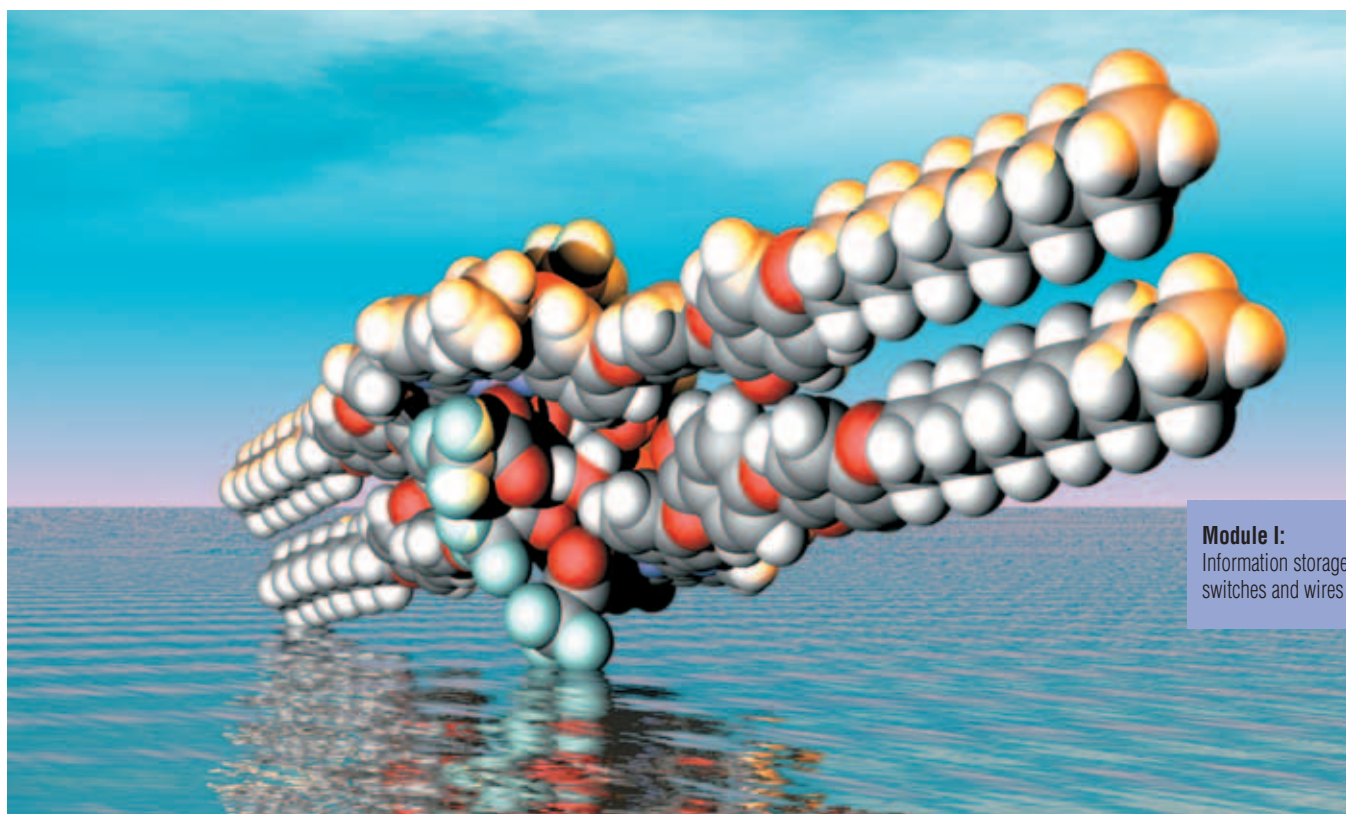
## Accommodation of lanthanides

“To counter this phenomenon, we thought of creating a molecule with a receptacle to accommodate these

particles,” explains Piguet. Two approaches were contemplated. A banana-shaped or semi-circular receptacle was developed in Geneva and a crown-shaped or completely circular receptacle was developed at Lausanne University by the group working with Professor Jean-Claude Bünzli. “Two different approaches which nevertheless complement each other,” adds Piguet when discussing this close collaboration.

“In both cases, we first had to synthesise the receptacles, and then we had to integrate the lanthanides. Now we have to think about what needs to be added to these basic units so that their supramolecular organisation is that of a liquid crystal.”

Field of application: Electronic displays.



**Module I:**  
Information storage, molecular  
switches and wires

Solid state structure of a rod-shaped lanthanide complex.

### An inductive approach

The Geneva approach is significantly different from the successive trial approach usually used in applied research, which consists in testing a large number of compounds in order to obtain one with good properties. "We are not looking for an application at any price. We want to understand the associated mechanism." According to the researcher, the approach is riskier but also more valuable. "If it doesn't work, we cannot just pick the next molecule. We have to understand what is not working and ask ourselves what changes need to be made to make it work. For us as academic researchers this inductive approach is exciting."

At the present time, Piguet's group is not collaborating with industry. "Industry expects us to show them that this works, which is understandable. Anyhow, it is advisable to wait before contacting a company. Academic freedom is very important for the development of new concepts. As our research develops, there will come a time when the question of large scale development will be raised. Collaboration with industry will then be more interesting."

### Something at the back of one's mind

While encouraging application-oriented projects, the Swiss National Foundation Programme guarantees academic freedom and time for thought. "This concept is ideal for me. I have never been able to conduct any research project without having an idea for an application, however distant this might be."

Some foreign groups are interested in the same subject. "I am happy with this, as I consider competition extremely positive and stimulating." However, the race has not yet really started. "It is still too early, the field is too new. As soon as the first encouraging results are obtained there is no doubt that more competition will appear." ■

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“Light driven molecular switches and molecular devices”

# Switchable molecules

As an architect of the infinitely small, Peter Belser, Professor at the Chemistry Department of Fribourg University, designs components required to exploit a promising field: molecular electronics.

**M**iniaturisation is no doubt the leitmotiv of present technologies. Of course, chemistry is also involved in this trend and the design of devices or units at molecular level is of major interest. “Supramolecular chemistry will enable us to move forward significantly,” reckons Belser. “Although molecules are only involved in simple reactions, supramolecular systems – assemblies of molecules – are capable of fulfilling much more complicated functions and may thus behave like real machines.” “The same phenomenon is also found at the macroscopic level,” continues the researcher. “Imagine a hair-dryer: it consists of a heating element, a fan and a switch... One of these components alone cannot perform the function of a hair-dryer. To achieve this function they must be assembled together.”

Fields of application: Molecular electronics, data storage.

## Peter Belser

Born in Basle in 1944. After an apprenticeship with Ciba-Geigy in Basle, and a chemistry diploma from the Engineering School in Winterthur – which has since become a member of the University of Applied Sciences of Zurich – Belser started studying chemistry at Fribourg University. He completed his studies with a thesis in 1979. Loyal to Fribourg, in 1981 he became Assistant Professor at the Institute for Inorganic Chemistry. In 1992, he was appointed Associate Professor. He has since developed research associating photochemistry with the chemistry of transition metals.



“Like a miniscule transistor.”

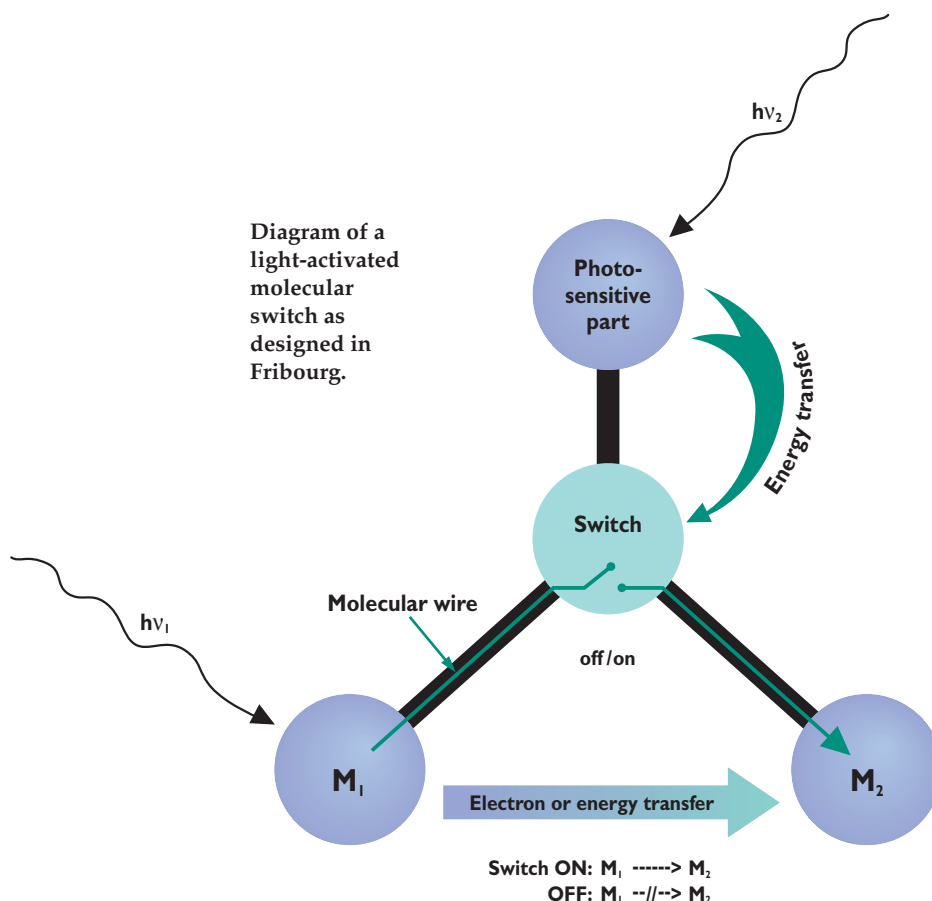
## Light-activated devices

Although it is original, the Fribourg project is not directed at developing a molecular hair-dryer. Its aim is to create switchable supramolecular assemblies. The specificity of such a system results from the fact that it may be found in two different states. An external stimulus enables switching from one state to the other. “If one of these two states is conducting and the other insulating, an electronic component is obtained, which operates not unlike a transistor, however, it is very much smaller,” explains Belser. “The potential is enormous but applications are still relatively far off.”

Therefore, the Fribourg team is simultaneously developing four substantially different supramolecular systems at a fundamental level. “Each system is dealt with by another member of the team.” Nevertheless, all four devices have similarities. “Each of these systems is activated or switched by light. Moreover, each system integrates an identical molecular brick on which absorption of light will occur, the photosensitive part. This molecule is a metal complex derived from the ruthenium tris-bipyridine family, a molecule discovered thirty years ago which, it was long hoped, had great potential for use in conversion of



Diagram of a light-activated molecular switch as designed in Fribourg.



solar energy into chemical or electrical energy."

### Molecular switch

When light is absorbed, excess energy accumulates in the photosensitive part. The excess energy is transmitted to the switchable part, the properties of which will have been changed. This change, which may be geometrical, chemical, or of another nature, forms the actual basis of what is called a switchable device.

One of the four devices developed in Fribourg may be used as a molecular electronic switch. In such a device, the energy transmitted by the photosensitive part is used either for forming or for breaking a chemical bond. When the bond is formed, the switch is in the ON position and an electron, i. e. a current, passes through the device. When the bond is broken, the switch is in the OFF position and the current can no longer flow through it. "The transition from the ON state to the OFF state is

caused by a beam of light. To form the bond, it is sufficient to expose the system to violet light (400nm) whereas exposure to orange light (600nm) breaks the bond."

### An internationally enviable situation

The Fribourg researchers are still working on other projects. "One of them may lead to a data storage system in which information would be written, read and erased by light. Another one could enable storage of solar energy."

Belser, who is a referee for various scientific journals, is well informed about the international situation: "Many groups are active in this field. Fortunately, we are able to maintain our enviable position because of the complexity of our systems and our long experience in synthesis." ■

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“Energy collection, transport and trapping by supramolecular organization of dyes in hexagonal zeolite nanocrystals”

# Antenna systems for light harvesting

**Professor Gion Calzaferri's research group at Berne University is building supramolecular antenna systems which absorb light and transmit the energy radiation-free to targeted acceptor molecules. In international comparison, the Bernese antenna system is one of the most successful. Possible fields of application are uses in sensors, solar cells as well as computer screens.**

**G**reen plants have antenna units consisting of a few 100 to 1,000 chlorophyll molecules. They capture light and transmit it to specific sites in the plant where chemical reactions are triggered. “In the laboratory we are producing a photonic antenna system which is constructed differently but with the same functionality and in this case we have come very close to the natural system,” states Calzaferri contentedly. His antenna systems capture light and transmit the energy from molecule to molecule radiation-free, that is without emitting free photons. To build the system, the Bernese group uses cylindrical zeolite crystals with lengths varying from 30 to 3,000 nanometres. The inside of the crystal consists of tubes which are exactly parallel. A crystal with a diameter of 600 nanometres consists of about 100,000 tubes. “We filled the tubes with dye molecules which are just

large enough to enter the tubes. A linear arrangement of coloured molecules results in each tube with specifically arranged colour zones in the whole crystal,” explains Calzaferri. In the meantime his researchers are so advanced that they are able to create any sequence of dyes they wish to.

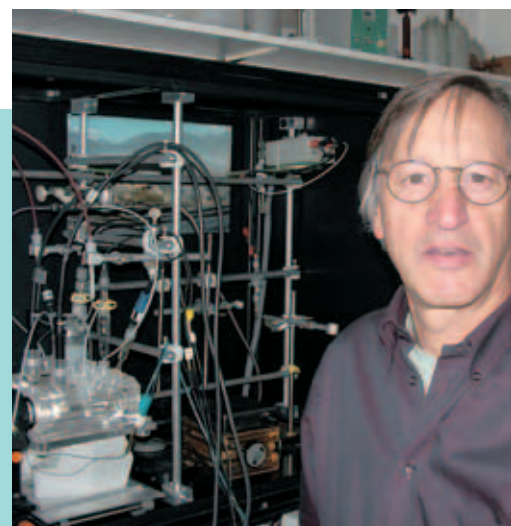
## Evidence for energy transfer

To prove experimentally that energy transfer takes place, Prof. Calzaferri is working with two kinds of photonic antennae (see figure). The “normal” type (left) contains a blue dye in the

central portion of the crystal; the crystals are closed at both ends with a red coloured area. In the “inverse” type, the sequence of colours is directly reversed. Now, if the blue areas are specifically excited with light, luminescence is observable not only in the blue areas but also in the red ones. “Using appropriate spectroscopic methods, we are able to show that the energy portions which are absorbed in the blue area migrate from molecule to molecule up to the red area and produce luminescence there,” summarises Calzaferri.

## Gion Calzaferri

Studied chemistry and obtained his doctorate at Fribourg University. Post-doctorate period with Edgar Heilbronner and Rolf Gleiter in Basle, followed by two years in pharmaceutical research with Ciba-Geigy. Gion Calzaferri has been working at Berne University since 1973, and has been Professor of Physical Chemistry since 1988. His scientific interests are directed at molecules organised into supramolecular structures; clusters and complexes in zeolite crystals; artificial antenna systems for absorption, conversion and capture of light; and the photochemical transformation and storage of solar energy.



“In functionality, we have come very close to the natural system.”

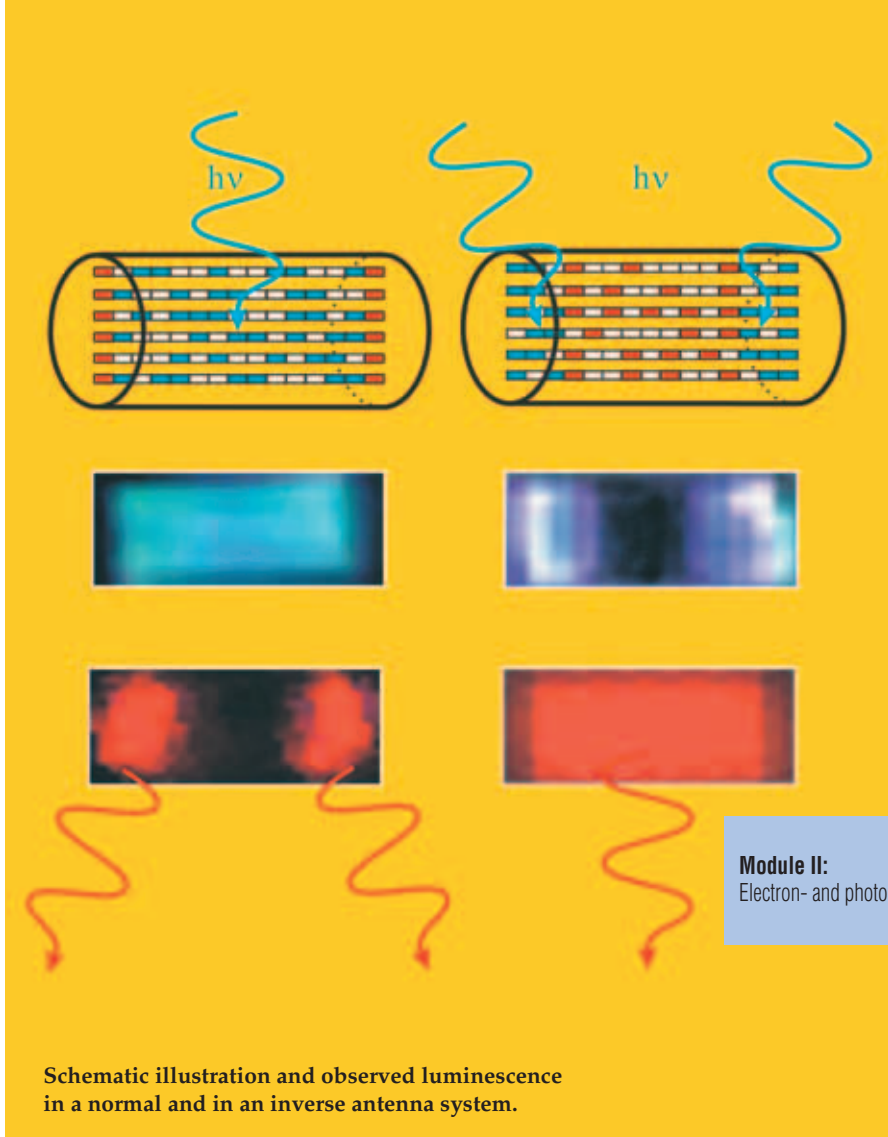
Fields of application: Sensors, solar cells, display screens.

### Simple, efficient approach

"There are numerous projects by renowned international research groups whose objective is to build antenna systems. However, our approach seems to be the simplest and the most successful by far. All the others involve a great deal of synthesis. As a result our work has attracted international attention," states the Bernese professor with satisfaction.

### Interesting prospects

One of the greatest challenges lies in placing an energy receiver optimally at the end of the tube to absorb energy i. e. on its surface, and to prepare it for further steps in the reaction. Calzaferri's opinion is: "If we succeed in this, light can be absorbed in the antenna system for example by 100,000 molecules and all of the energy collected may then be focussed onto one molecule on the surface. This corresponds to an amplification factor of 100,000. This might be interesting for use in detector sensors." Another application for the antenna system is ambitious, but conceivable; a thin layer might be placed on solar cells or the systems could be used in computer screens. A milestone on the long path to actual applications was the filing of the first patent for North America in November 2000 in collaboration with Unitectra.



Schematic illustration and observed luminescence in a normal and in an inverse antenna system.

### A good team

Calzaferri and his co-workers have made quicker progress than expected. His strategy for the next phase of the project is targeted at building effective dye molecules. The composition of his group, both physics-orientated and experimental chemists, is an ideal basis for achieving further success. "Good training as a chemist or an experimental physicist is important for us. There is no pure synthesis doctoral work available here," he confirms. For analytical studies, he co-operates with Prof. Alfred Meixner, Siegen University (Germany), Dr. Robert Pansu, Ecole Supérieure de Cachan, in Paris, as well as with Prof. Tjeerd Schaafsma, Wageningen University (The Netherlands). ■

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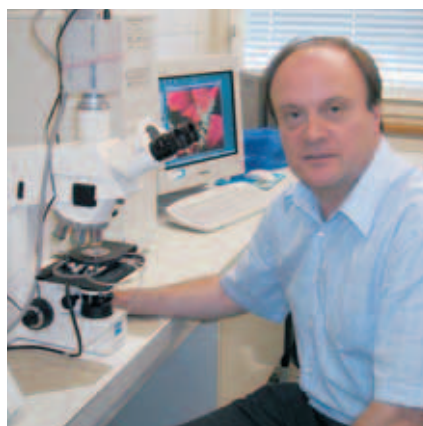
# Supramolecular strength through unity

Group the properties of three known chemical systems together in a single material: this is the goal that Professor Robert Deschenaux and his team at Neuchâtel University's Institute of Chemistry have set themselves. Although applications may be envisaged, their supramolecular approach is still in the realm of basic research.

What makes a supramolecular assembly unique is the elaborate function it acquires from the various molecular units from which it is made up, functions the components do not have in isolation – the chemical equivalent of “strength through unity”. Deschenaux, perhaps inspired by this maxim, has the idea of grouping the properties of polymers, of liquid crystals and of ferrocene in a new material.

The idea is attractive, however, its implementation is no triviality. “This is where supramolecular chemistry comes in as a kind of molecular sociology,” explains Deschenaux. “Proper cohabitation of each of the units forming the supramolecular material needs to be ensured. If a particular molecule is assembled in a certain manner this gives rise to a liquid crystal organisation, however, a slight change in the molecule may be enough to prevent this arrangement. We need to understand the reasons for this.”

Fields of application: Electronic displays, molecular electronics.



“Basic research in fields of application.”

## Robert Deschenaux

Born in Le Locle in 1957. He studied chemistry at Neuchâtel University before obtaining his Ph.D. in 1983 with a thesis on inorganic chemistry dealing with copper complexes. After three post-doctoral appointments including one in Prof. Jean-Marie Lehn's group in Strasbourg, he worked with Ciba-Geigy for a little more than a year. He learned a great deal during this practical period in industry. Since 1991, he has been Full Professor for Organic Chemistry at Neuchâtel University. All his research work deals with organised supramolecular materials.

## Ferrocene and co.

The first stage in the Neuchâtel project consists in forming the molecular unit which will be the basis for the projected material. The molecule contains ferrocene. Because of its unique structure, an iron atom sandwiched between two organic cycles, ferrocene has special electrochemical and optical properties. “We hope that these properties will also be found in the macroscopic material,” adds Deschenaux.

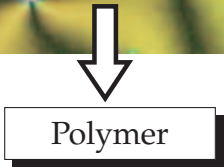
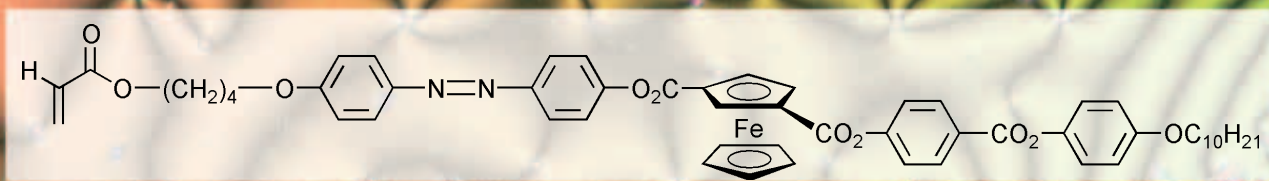
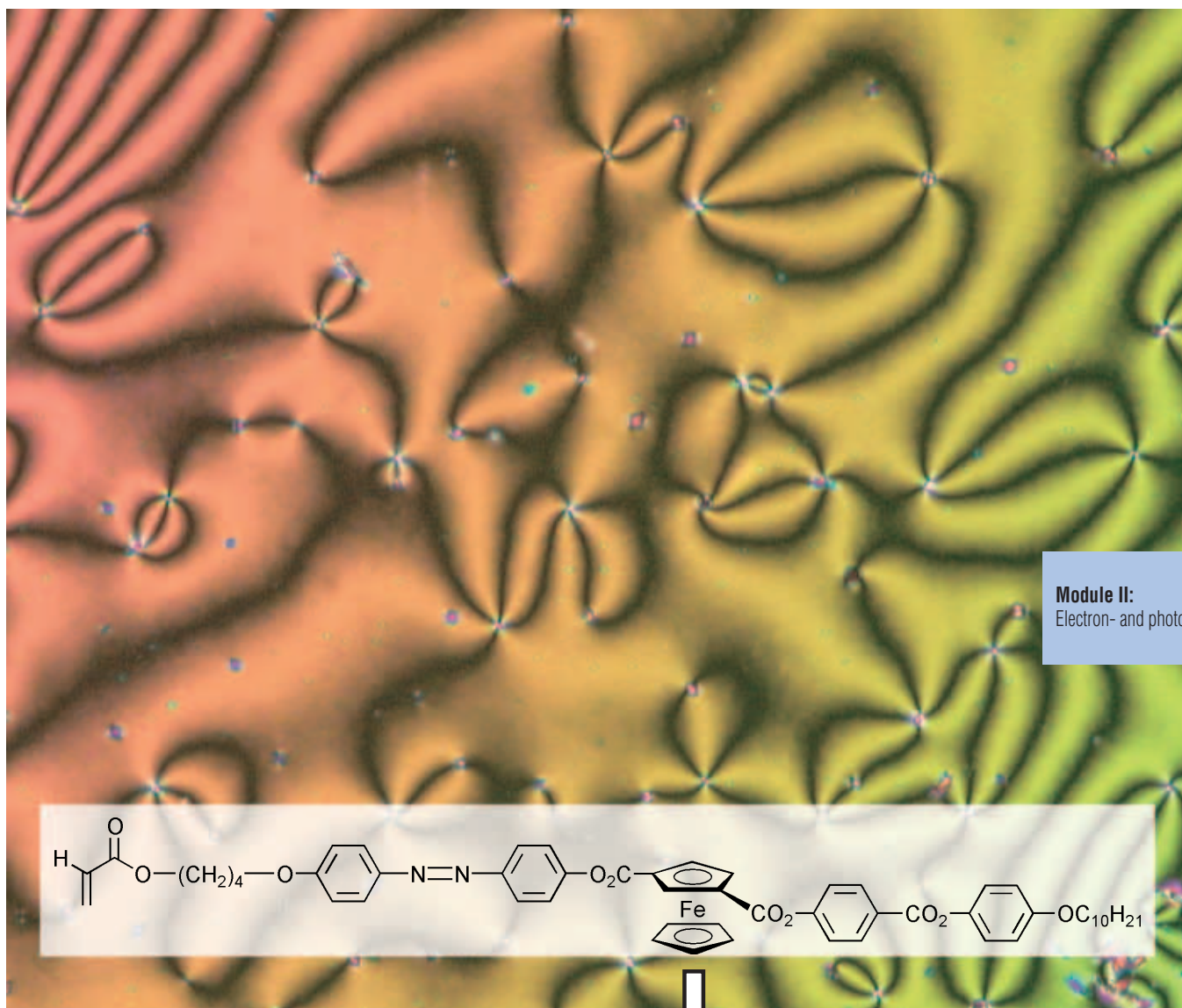
The other two components present in the basic molecular unit should allow the molecule to polymerise in the first step and then to form a liquid crystal in the second one. “At the moment, we are examining the relationship between the molecule's structure and its organisation at supramolecular level. After these steps are completed, we will examine the relationship between the organisation of the material and its properties.”

## Nothing left to chance

“Another approach would be to synthesise a large number of molecules until we obtain one which has the

desired microscopic and macroscopic properties,” explains Deschenaux. However, this is not the option being pursued in Neuchâtel. “We do not start with a molecule and say: ‘Let's see what it can do.’ Rather we wish to obtain a specific property and we are looking for the molecule which should enable us to obtain it.”

Therefore this specific property was defined at the very start of the project. “We want to develop a switchable liquid crystal polymer material,” explains Deschenaux. “This type of material may adopt two different states. When it reacts to an external stimulus – e.g. absorbs light or a voltage is ap-



Texture of the nematic phase exhibited by a ferrocene monomer observed through a polarised light microscope. This monomer will be used to obtain liquid crystal polymers.

plied at its ends – the material switches between two states.”

### Numerous applications...

This type of material should open up the potential for numerous applications in various fields such as electronic displays, bioanalytics, data storage... “I define my work as basic research in fields of application. Industrial collaboration is quite conceivable. Our role, however, is to identify the fundamental principles governing the materials and their properties, industry’s is to develop technologies using them.”

### ...and collaborations

The field of liquid crystals is very vast. “We cannot cover all aspects,” notes Deschenaux. “We are therefore collaborating with other Swiss groups and with foreign groups, especially to determine the three-dimensional organisation of the material using X-ray diffraction. In Neuchâtel, our main task is to design the molecules.” ■

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# DNA: the silicon of the future?

**At the Institute for Organic Chemistry at Basle University, Professor Bernd Giese’s team is studying the conductive properties of DNA. The stakes are high in view of the anticipated slow but unavoidable transition from microelectronics to nanoelectronics.**

In harmony with Moore’s famous law, components in electronic devices have undergone a drastic reduction in size during the last ten years. This trend to miniaturisation is bound to continue. Therefore, it has become absolutely necessary to understand how electron transfer takes place at molecular level; this transfer is often very different from that from which microelectronics has benefited up to now.

In view of this, the Basle team is investigating charge transport in DNA, the carrier of genetic information. “The primary goal of this project is to find out whether DNA may be used as a medium for conducting electricity, like an electric wire in fact,” explains Giese. “The question has been the subject of lively discussion since the early nineties.”

## A very important discovery

The Basle team’s study is progressing well. “In an article recently published in the journal *Nature*,” relates Giese, “we describe long distance transport of a positive charge in DNA. Earlier, we believed that DNA only conducted over very short distances. We showed, however, that conductivity decreases up to a specific distance, thereafter conductivity remains constant. The charge transfer rate is then no longer high, of the order of a microsecond, but it is very efficient.”

This discovery is very important for the scientific community. It opens interesting prospects for the use of DNA by providing a new interpretation of charge transfer mechanism. There is a long way to go before we can say whether DNA can be used in electronics and whether it will replace silicon in future nanoelectronics, as certain scientists already believe. Giese is adamant: “We are still far from being able to answer the question. We are still very much at the basic research stage.”

## Beneficial charge transfer

The information provided by this study of DNA is also significant to our understanding of a totally different phenomenon. The charge transfer mechanism in DNA gives us insight into illnesses like Parkinson’s disease or Alzheimer’s, which are linked to damage to the DNA caused by oxygen. “As is so often the case in science, basic research leads to findings relevant to other fields.”



Schematic illustration of charge transfer in DNA.

Field of application:  
Molecular electronics.



“Research does not always lead to what we originally expected.”

### Bernd Giese

Born in Hamburg in 1940, Bernd Giese studied chemistry at the Universities of Heidelberg, Hamburg and Munich. In 1969, he was awarded his doctorate at the University of Munich for a thesis in the field of organic chemistry. In 1989, he was appointed Full Professor at the Institute for Organic Chemistry at the University of Basle. His research work relates essentially to radical reactions in biological systems.

**Module II:**  
Electron- and photon- transfer

Because of the high oxygen concentration and the perpetual presence of light, the environment in which we live is very aggressive. This constellation may cause oxidation of certain biological molecules in our organism. If DNA is affected by this phenomenon, a mutation may result. A mutation in the DNA coding sequence would have serious consequences. On the other hand, if the positive charge could be displaced by charge transfer to a non-coding sequence then the mutation might occur without any harmful consequences. It is assumed that charge transfer protects DNA from harmful mutations. This very new theory is called “cathodic protection of genes” and remains a hypothesis in scientific circles.

### Dreams of applications

As one of the long term goals of this research is to use DNA in nanoelectronics, Giese’s main goal is to acquire a wealth of fundamental information on the structure. “As chemists, we attempt to understand our environment at the molecular level. Later, we may be able to dream up applications.” This being said, applications may not be that far off as a number of scientists are speculating whether DNA will replace silicon in the future. Giese and his team intend to make a significant contribution to this objective. ■

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# Where chemistry and physics meet

Hans-Joachim Güntherodt, Full Professor at Basle University's Institute for Physics, utilises the potential of scanning probe microscopes to develop supramolecular assemblies capable of contributing to progress in the new field of molecular electronics.



“The idea is to replace integrated circuits with molecular electronics.”

## Hans-Joachim Güntherodt

Born in Suhl in 1939. He studied physics at the ETH Zurich, finishing with a thesis on the electrical properties of liquid metals. In 1974, he was appointed Full Professor at Basle University. In the general framework of his research, he is applying recent developments in scanning probe microscopy to physics, chemistry and biology. Since 2001, he has led the Swiss National Centre for Competence in Research “Nanoscale Sciences.”

“Browsing through the history of electronics, we first encounter valves,” explains Güntherodt. “They were progressively replaced by transistors and then finally by integrated circuits, ever smaller and more powerful, which are presently still in use. However, the process of miniaturisation cannot go on ad infinitum. A number of scientists, including ourselves, intend to replace these present circuits with molecular electronics.” Researchers are searching for switchable molecules which are able to switch between two states or, in analogy to computer science, switch between the 1 or 0 position. “Recently, a collaboration between the University of California, Los Angeles, and Hewlett Packard resulted in creation of such a molecule called rotaxane. But nobody really knows which molecule will best fulfill this switching function. This remains an open question.”

## Which family of molecules is the right one?

For the Basle group, the answer will not be found without close collaboration between branches of chemistry

Field of application:  
Molecular electronics.

and physics. “Experts in synthesis chemistry – Professor Constable, formerly at Basle University and presently in Birmingham, as well as Professors Diederich and Seebach at ETH Zurich – have been preparing various molecules for us capable of meeting our needs,” continues Dr. Bianca Hermann, who is preparing a habilitation thesis in Güntherodt's group and is also scientific leader of this project.

“We are presently investigating four different families of molecules: dendrimers, or ‘cascade molecules’ because of their very numerous ramifications; ligands of fullerenes; metal complexes; dye complexes. Each of these four families has interesting electronic properties. We still do not know which family is best suited to our project. Depending on the result, we will perhaps focus on only one of them.”

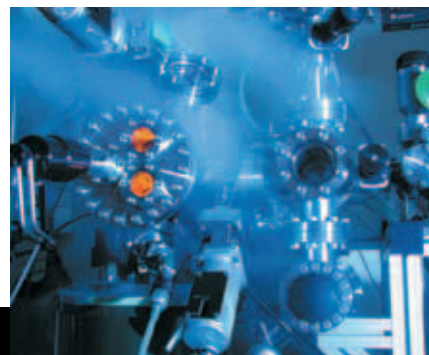
## Supramolecular films

And what part do the physicists play in the project? “As soon as the molecules have been obtained by the

chemists, our work consists in assembling them into supramolecular film-like constructions,” explains Hermann. These molecules, that are too large to be evaporated, are dissolved and then deposited on a conducting surface.

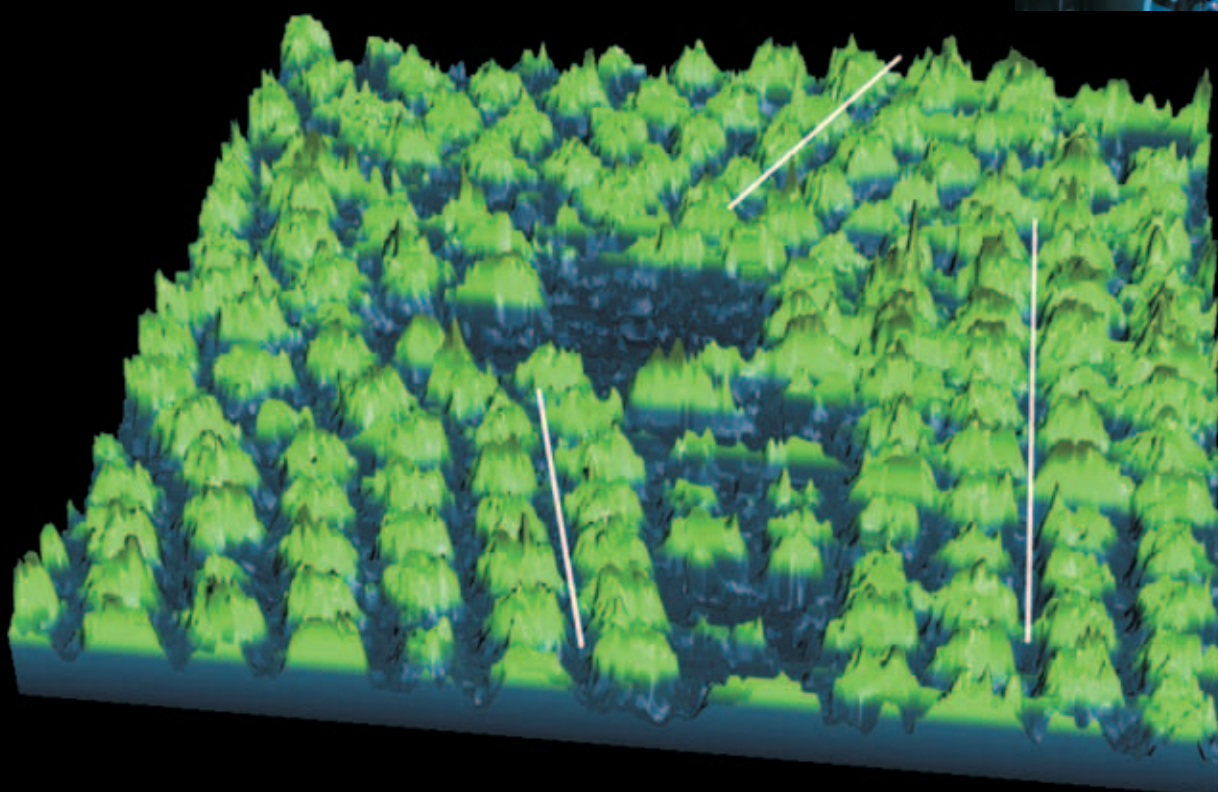
The supramolecular arrangement is then viewed using scanning tunnel microscopy or atomic force microscopy, ideal instruments for the nanoscopic world which were developed in the early eighties at the IBM laboratories in Rüschlikon. “We are able to see the structure of our films at molecular level. Depending on what we see, we shall subsequently try to develop an effective methodology for building these assemblies.”





**Module II:**  
Electron- and photon- transfer

The structure of materials at the molecular level may be observed and changed with scanning probe microscopes.



**A billion molecules per cm<sup>2</sup>**

However, the originality and the potential of the Basle project are not limited to synthesis and characterisation of supramolecular films. In a second phase, we anticipate using scanning probe microscopy not only to view the film but also to modify. "The stimulus for switching a molecule on the film may come from the tip of the microscope," adds Hermann. "In this way, it might be possible to change not only a set of molecules, but one

single molecule and this in a specific manner."

Using a film like this consisting of a billion molecules per cm<sup>2</sup> in a data storage device would increase its capacity considerably. "The expectations roused by such a system are high, research is, however, still only at a very fundamental stage," moderates Güntherodt. A stage which nevertheless justified the recent trip to Basle by researchers from the Japanese firm Sony. ■

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# Tiny supramolecular columns for flat screens

The chemists have something to say in the development of new generations of flat screens. That, at any rate, is the view of Titus Jenny, Associate Professor at the Department of Chemistry of the University of Fribourg.

In the beginning, there were cathode-ray tubes, the first of which was made in 1911 by the Russian, Boris Rosing. And still today, some television and computer screens work on this principle, as developed at the start of the 20th century. These are the screens known as CRTs (Cathode Ray Tubes). “The problem,” as Jenny explains, “is that it is not conceivable, because of weight and size issues, to build large screens using this principle. Besides, their energy consumption is high.”

That is the reason why research on flat screens has accelerated strongly in recent years. The methods developed up to now are either very costly, or not very satisfactory, or indeed both in many cases. “There is a challenge to be accepted, and that is what motivates us.”

## Field emission screens

The Fribourg group takes its inspiration from what are known as field-emission screens. The principle on which they work is similar to that of CRT screens. Instead of having just one large cathode ray tube – or one per colour – the screen consists of a multi-

Field of application:  
Electronic displays.



## Titus Jenny

Born in Arlesheim (BL) in 1950, he studied chemistry at Zurich University. It was also in Zurich that he obtained his doctorate, for a thesis project half-way between metallo-organic chemistry and analytical chemistry. Since 1992, he has been Associate Professor at the Institute of Organic Chemistry of the University of Fribourg, where he is conducting research in synthetic metallo-organic chemistry employing a wide range of analytical methods. In general, these research topics are inspired more by physical chemistry than by biochemistry.

“I like inventing things.”

tude of microtips, each of which acts like a cathode ray tube. From these microtips – that are currently made of metal – electrons are released which then illuminate the screen.

## Close to application? Yes...

The method is known and seems to work. “It is arousing increasing interest in the industry,” adds Jenny. It is however, difficult to reproduce in technical terms. It is a very delicate matter to get the metallic tips uniform, essential because of the sensitivity of the human eye. “That is where supramolecular chemistry comes in. We would like to make the microtips from molecules that would have the special property of stacking themselves automatically into columns. Theoretically the supramolecular properties of the

columns should ensure the uniformity that is currently a problem.”

Furthermore, a team of physicists working with the Fribourg group as part of the project have recently demonstrated the field emission property with similar structures namely, nanotubes. Unfortunately, it is very difficult to make nanotubes in a structured fashion. “With the right molecule and a touch of supramolecular chemistry, we should get supramolecular structures aligned in the shape of a column.”

## ...but

All seems to be for the best in the best of worlds. But Jenny is not Voltaire’s Candide. “For now, we are not sure whether the molecules can be stacked into isolated columns,” Jenny explains.

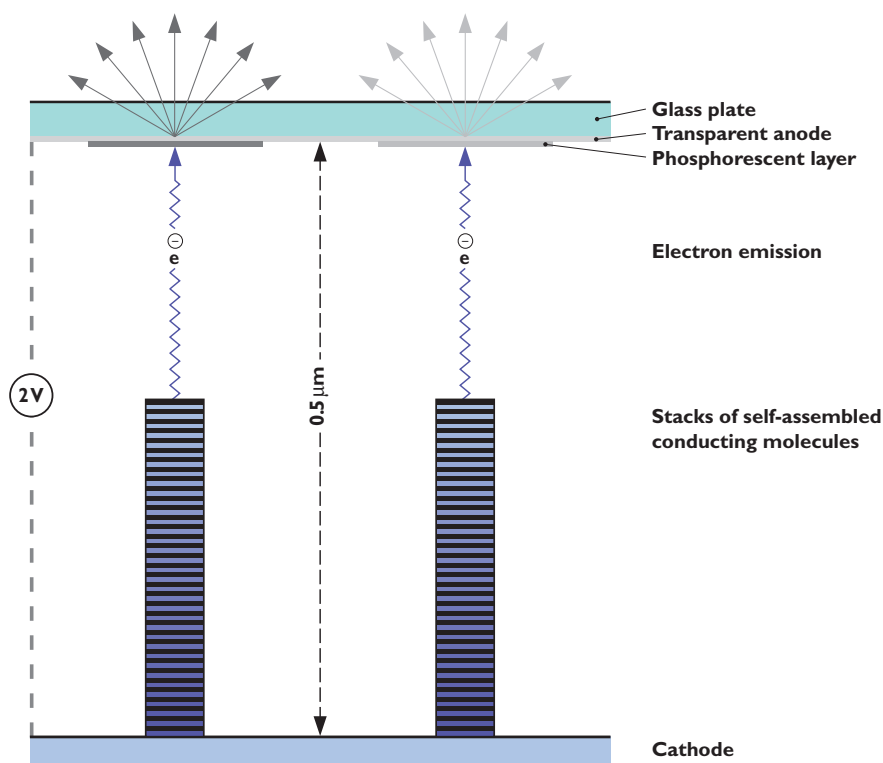


Diagram of a field emission screen as developed by the research group in Fribourg; using supramolecular chemistry it should be possible to manufacture uniform tips.

“We are studying various molecules that might produce such an arrangement. All of them have an aromatic ring that should direct the stacking.” That’s all we are going to be told. “It’s an idea that could easily be copied.” “Once we have made some supramolecular assemblies from such molecules, we will have to check again that the assembly is really in the form of a column. We will then be using well-known analytical techniques such as solid-state nuclear magnetic resonance, scanning tunnel microscopy or atomic force microscopy.” Producing stacks from such molecules does not necessarily mean there will be field emission, however. “We still have to test for it. If there is emission, we will then have, in collaboration with physics, to create the substrate to which our micro-columns will be attached. The substrate should be a conductor and should contain anchorage points to which our columns should be attached.”

Finally, marketing can be contemplated. The path is clearly drawn up to the stage of obtaining the product. “We should not be under any illusions however,” Jenny emphasises. “Although every stage may be well defined, each stage is ridden with numerous uncertainties.”

#### Atoms hooked by physics

This project is the outcome of a meeting between a chemist and a physicist. “After having followed a lecture by a physicist explaining the problems that he was having in trying to get diamonds to grow on a solid substrate, I started to look at the question from the point of view of a chemist,” Jenny explains. “We met regularly from then on: he was introducing me to the study of field emission and I was providing him with chemical solutions.” Many things happen by chance: NRP 47 was launched at the same time. ■

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# Nanobarrels “à la baguette”

**At the Department for Organic Chemistry of Geneva University, Professor Stefan Matile and his team have developed the first method for synthesising artificial barrel-shaped chemical structures. Just like those on the macroscopic scale, these barrels also provide space which may contain various substances. Moreover, as the ends of the barrels are open they may be used as channels for transport of molecules. The potential for applications is very promising.**

“For this project, I have drawn my inspiration from the cells which populate our body,” relates Matile. The Geneva group’s interest centres on small channels, called ionic channels, distributed on the cell membrane which ensure exchange of matter between the inside and the outside of the cell.

“These ionic channels fulfil a vital function. Used outside their natural environment, the barrels – the channels extracted from the membrane look like open-ended barrels or kegs – may fulfil a thousand other functions,” adds Matile. Consequently, in view of their dimensions these barrels or nanobarrels really are of great interest to the scientific community.

Fields of application: Gene therapy, chemical detectors, catalysis.

## Considerable prospects for applications

Even before Matile’s work began, nanobarrels had already been obtained in the laboratory. Like their natural counterparts, they are composed of large biomolecules, chemically modified proteins in fact. The Geneva team was first to synthesise artificial barrels from simple rod-shaped organic molecules. By the way, these rod-shaped molecules are also sometimes called “baguettes” after the well-known French bread – hence the expression chemistry “à la baguette” which Matile likes to use.

In the supramolecular assembly these rod-shaped molecules form the staves of the barrel. The inner diameter of the barrel varies between 2 and 3 nanometres, “large enough to contain a DNA double-helix structure for example, which may be interesting in gene ther-

apy.” But these structures may have further uses in other fields such as in catalysis, pharmacology, chemical detection, and drug transport... “From what we know today, a large number of applications are conceivable. However, none have yet been realised.”

## Great expertise in synthesis

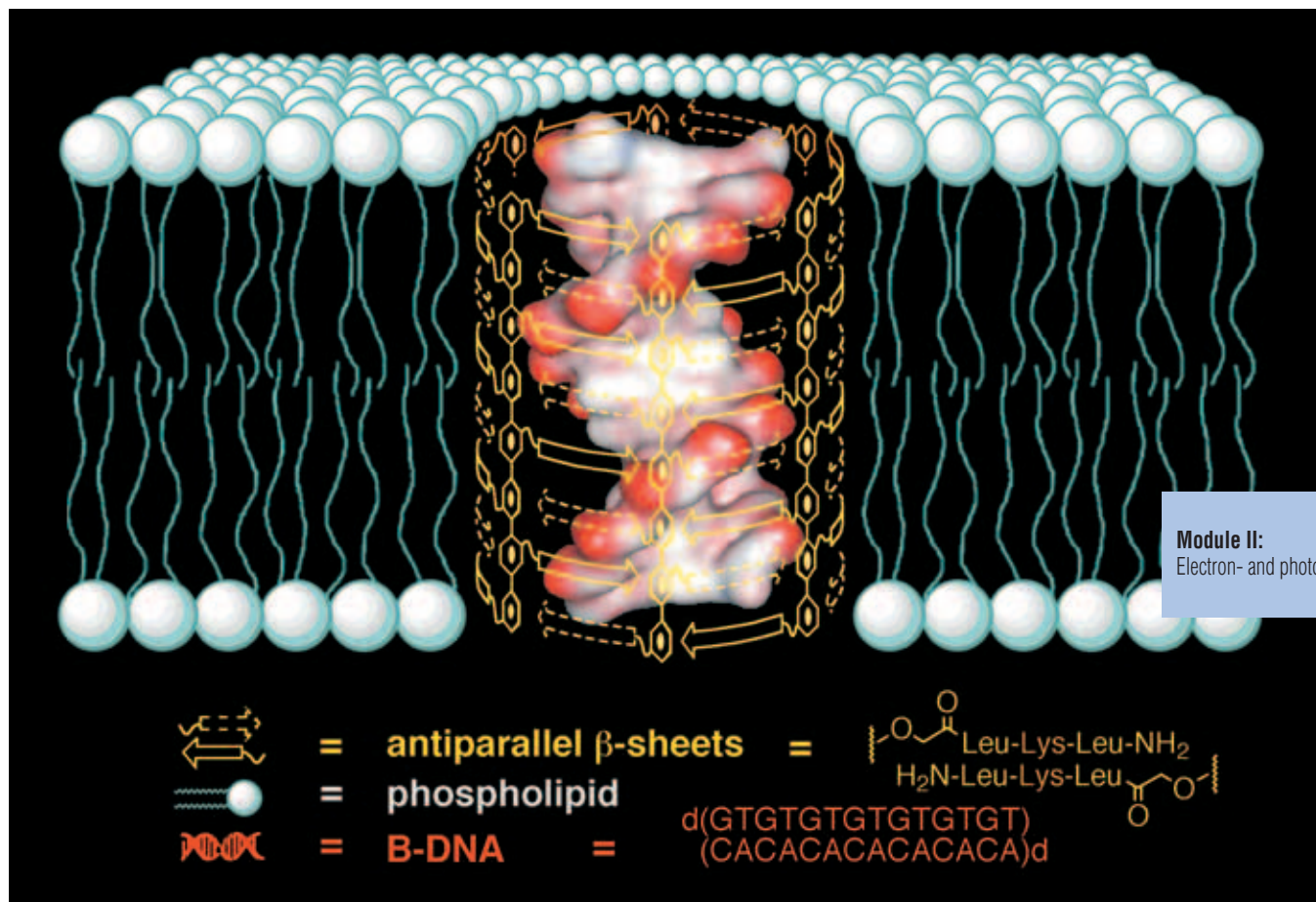
In the meantime, the Geneva group has made further progress in synthesis. “Today, with the method developed in my laboratory, we are able to modify the external and internal properties of the barrels,” explains Matile. “The potential of our nanobarrels lies in our ability to control both the internal and external properties.”

“We have created the field and so we are the leaders in it.”

## Stefan Matile

Born in Zurich in 1963. He studied chemistry at Zurich University. He also obtained his Ph.D. with thesis work in the field of bioorganic chemistry. During a post-doctoral stay at Columbia University in New York, he worked on rod-shaped molecules for the first time. In 1996, he became Assistant Professor at Georgetown University in Washington DC where he started to develop the field of bioorganic chemistry “à la baguette”, as he likes to call it. Since 1999, Matile has been Assistant Professor at the Department for Organic Chemistry of Geneva University.





By changing the external properties of a nanobarrel, it can be inserted into another medium such as membranes. Changing the chemical composition inside the barrel increases selectivity on the molecules which may enter the barrel.

### Collaboration with industry

Now that the Geneva group has mastered synthesis of the nanobarrels, it intends to make an inventory of all the possible fields of application. "However, development is outside the competence of academic laboratories. This task should be taken up by industry," states Matile explicitly.

"A collaboration with industry would be interesting because both parties would benefit," he continues. "We perform the synthesis and we provide examples demonstrating the possible fields of application. Then industry, which also has talented researchers, takes over development. We are able to stand by with advice and help."

Matile's group is comfortably installed in the field of nanobarrels. "We created this field and so we are the leaders in it," concludes the researcher. ■

One of the supramolecular barrels developed in Geneva: large enough to contain a DNA double-helix structure.

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# Uniting nanocrystals and biomolecules

An assembly of nanocrystals and biomolecules: this is the vision of Claus Duschl, lecturer at the Laboratory of Physical Chemistry of Polymers and Membranes at the Swiss Federal Institute of Technology Lausanne (EPFL). These new composite materials have optical properties which may be changed by a biological stimulus – an interesting prospect in the very promising field of bioanalytics.

Interesting properties at the nanoscale are not necessarily interesting at the human scale. Transition from the molecular world to the macroscopic world is not a trivial matter. The researchers in Duschl's team experience this daily. They wish to take advantage of the enormous potential represented by nanoparticles at the human scale. “The purpose of this project is to combine nanocrystals and biological molecules in order to form composite materials with optical properties useful in bioanalytics,” explains Duschl.

## Nanocrystals

Tiny crystals with highly interesting properties are the basis for Duschl's project. Because of their diameter, which varies between 2 and 6 nanometres, these particles are also called

“I observe chemical and biological systems with the eye of a physicist.”



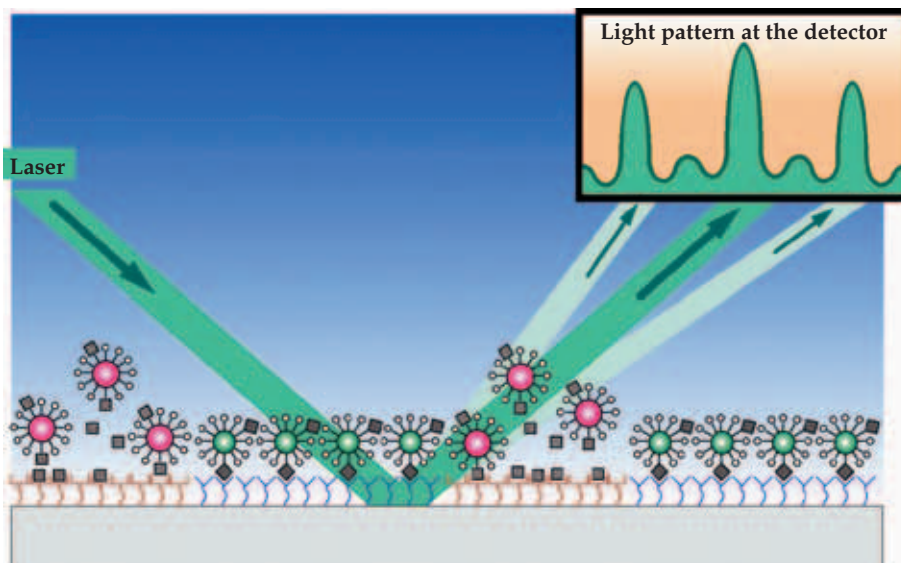
## Claus Duschl

Born in 1954 in Eggenfelden, Germany. He studied physics at Munich University. He also obtained his Ph.D. after completing his thesis in the field of spectroscopy on organic films. He then had a post-doctoral stay at the Institute for Biotechnology of Cambridge University. In 1994, he arrived at the Laboratory of Physical Chemistry of Polymers and Membranes of the Swiss Federal Institute of Technology Lausanne (EPFL), where today he is conducting investigations in the field of spectroscopy and optics on organic surfaces.

nanoparticles or nanocrystals due to their crystalline nature. At these dimensions, these materials are governed by the laws of quantum physics which seem strange when first encountered.

The effect of these laws is clearly seen when we look at the optical properties of the nanocrystals. For example, they emit coloured light which changes with the size of the crystal: a crystal with a given composition and a diameter of 2 nanometres will emit green light, the same crystal emits red light if it is 5 nanometres in diameter. A crystal with a given size emits a given colour of light. “Unless of course the environment of the nanocrystal changes,” points out Duschl. “Then, the emission of light is changed. In other words, information can be obtained on the environment from changes in the emission of light from the nanocrystal.” These nanoparticles are thus very promising candidates for detecting and labelling chemical and biological reactions.

Field of application: Bioanalytics.



Different nanocrystals enveloped by biomolecules align themselves selectively on a surface by means of molecular recognition. The green nanocrystals form a network which modulates the reflected laser light.

### ...enveloped in biomolecules

However, the nanocrystals themselves need to be enveloped in biomolecules. The envelope enables nanocrystals to self-assemble via molecular recognition. This composite material needs to have new properties different from those of isolated particles as in such structures each particle is sensitive to its neighbour. "These are the new properties which we are interested in studying. Furthermore, as soon as a foreign biomolecule approaches it begins to interfere with the composite material again via molecular recognition. We thus have a new concept for a biological detector."

### Vast prospects

"The prospects opened up for use of these composite materials in the bio-analytics sector are very promising," highlights Duschl. "Some companies are already interested in our research." Indeed, an arrangement of composite materials on a surface would be an excellent means for studying the active ingredients of chemical compounds for pharmaceutical applications. It would be possible to determine quickly which active ingredient reacts with which type of biomolecules. "However, in spite of the vast prospects for application, there remain a number of fundamental points

which need to be explained." This is precisely the goal of the Lausanne group. Although synthesis of these nanoparticles has been relatively well mastered, depositing a layer of biomolecules on the surfaces of nanoparticles is more problematic. "This is in part due to the large curvature of these particles, which have diameters between 2 and 6 nanometres. To be perfectly efficient, the layer also has to be sufficiently dense, homogeneous and stable. Its influence on the optical properties of the nanocrystals also needs to be better understood."

### Stimulating competition

"Some competition seems to be emerging in this field," points out Duschl. "But this is very positive, as this means that the field is attracting interest and obviously shows more potential." Initial research in the field was conducted by mineral chemistry specialists. They were familiar with nanocrystals but less so with biomolecules. "Our advantage is that we have expertise in both of these fields," concludes Duschl. ■

**Module III:**  
Sensors and diagnostic tools

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# At the frontier between the supra and macroscopic worlds

At the Swiss Federal Institute of Technology's (EPFL) Laboratory of Photonics and Interfaces in Lausanne, Professor Michael Grätzel and his team are developing surfaces with remarkable optical and electronic properties. The potential for applications is wide extending from the conversion of solar energy to information storage systems.

The interest of the Lausanne group centres on a methodology to create a link between supramolecular properties and the macroscopic world rather than on a supramolecular machine provided with a specific function as for this group all that glitters is not gold!

All that glitters? “Molecules composed of two electronically or optically active parts on the one hand, and on the other, very rough semi-conducting nanocrystalline surfaces,” explains Grätzel. Gold? “This is the material resulting when these molecules are assembled. It should be able to amplify, transduce and store photochemical and electrochemical signals,” continues the researcher.

Fields of application: Molecular electronics, information storage.



**Michael Grätzel**

Born in 1944 in Dorchemnitz in Germany. He obtained his chemistry diploma at the Free University of Berlin in 1968. He then joined the Technical University in the same city where he obtained his Ph.D. in 1971 with a thesis relating to the kinetics of fast reactions. In 1977, he was appointed Professor for Physical Chemistry at the EPFL. His fields of research are artificial photosynthesis (construction of a new type of photovoltaic battery, catalytic reduction of carbon dioxide), bioelectronics, catalysis as well as the preparation and application of nanocrystals.

“Aim for first class scientific publications rather than applications.”

## Increase the yield of solar cells

Using the materials developed in Lausanne it may be possible to convert solar energy into electric energy more efficiently. Conventional solar cells convert light into electricity by utilising the photovoltaic effect of semiconductors. “They carry out two functions simultaneously; they absorb light and separate electrical charges. Very frequently, if the material is not very pure, the charges recombine too early reducing conversion yield,” explains Grätzel.

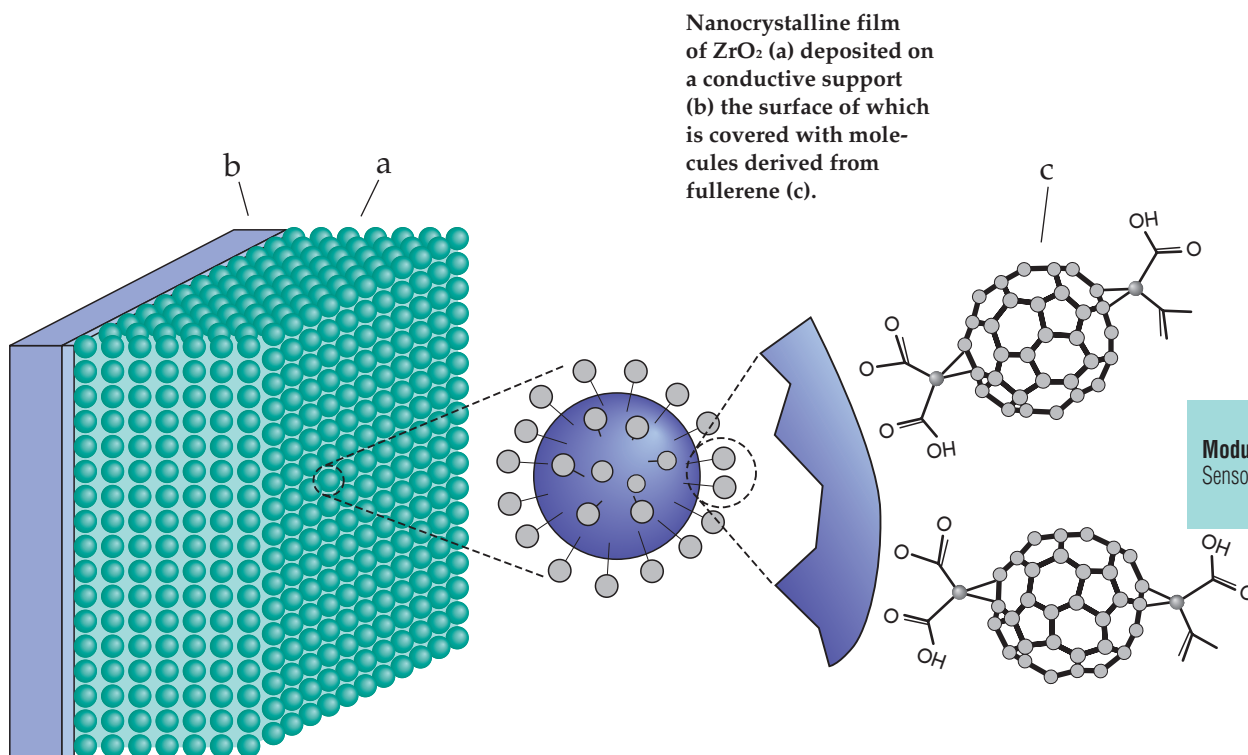
With the materials developed within the scope of this project, the light absorption function and those involved in separating electrical charges may be differentiated. “They thus hold out hope of a significant increase in the yield of solar cells, and, as they are simple to manufacture, a reduction in the cost of solar electricity.”

## Molecules grafted onto nanocrystalline particles

Absorption of light is taken care of by a layer of molecules grafted onto the surface of the semiconductor. The chromophore part of the molecules is excited by absorption of a photon of light. As a result, an electron is injected into the attached semiconducting particle. The second electrochromic part of the molecule prevents the electron returning hindering rapid recombination of charges.



# molecular



**Module III:**  
Sensors and diagnostic tools

The light absorption capacity of a monolayer of these molecules would be very low. To remedy this problem and to achieve a significant conversion yield, the surface of the semiconductor is not planar. "It is like a very rough porous film. Thus, the surface area of the system is increased and greater absorption of light results leading to more effective conversion into electricity," points out Grätzel.

## Other applications

Using this type of material it may be possible to manufacture optical information storage systems. In this type of structure, semiconducting nanoparticles and the molecules surrounding them are dispersed in a polymer. When exposed to photo-excitation,

these particles become negatively charged. They thus enable data recording at the nano level, as well as the possibility of reading and erasing information.

"This NRP 47 project provides us with more freedom to conduct basic research," states Grätzel freely. "Admittedly we have an idea for an application, but only in the long term. This is a very comfortable situation, because, to get established in the scientific community, marketing is not the main goal, rather, you need to aim for first class publications." ■

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# Emergence of supramolecular kinetics

**The association and dissociation rates inside a supramolecular assembly are fundamental parameters which need to be understood and controlled before products can be marketed. Werner Nau, Professor at the Institute for Physical Chemistry at Basle University, is one of the pioneers in this field which is called supramolecular kinetics.**

“If I want to buy a racing car, I first look at its top speed. In supramolecular chemistry, where researchers develop functional machines, they should think similarly,” points out Nau. “However, among all the scientists active in this field, very few of them are interested in the speed at which their machines will run. This question will soon be crucial.”

Imagine a supramolecular machine used to control targeted drug release in the human body. Of course, it is important to have detailed knowledge of the structure of such a machine. But it is also fundamental to know the rate at which the drug will be released as its efficiency depends on the speed at which it functions. This field of study is called supramolecular kinetics.

Fields of application: Supramolecular machines, pharmacology.

## Fluorescent detectors

After searching for a very sensitive analytical method enabling them to observe a reaction taking place on one single molecule, the Basle group selected fluorescence spectroscopy. “This method uses fluorescent molecular detectors, synthesis of which is the main purpose of our research. When they are inserted into the core of a system to be studied, the light they emit is strongly influenced by their environment; thus they provide detailed information about it,” explains Nau.

These fluorescent detectors have to differ depending on the system. The Basle group designs and modifies them and has acquired substantial expertise in synthesis. “We have developed detectors which remain in the fluorescent state for a very long time, something of the order of one microsecond. This is the longest fluorescence lifetime ever observed in organic detectors. Using them, we can study both fast and slow reactions.”

## Host-guest system

The Basle team is applying its methods to two types of supramolecular systems. The first, the simplest one, only consists of two molecules. A molecule called a host molecule may accommodate another so-called guest molecule. The term host-guest system stems from Nobel Prize Laureate Donald J. Cram, one of three chemists honoured in 1987 for work in the field of supra-



### Werner Nau

Born in Fulda in Germany in 1968. He studied chemistry at Würzburg University. After having completed an M.Sc. at St. Francis Xavier University in Canada, he returned to Würzburg where he obtained his Ph.D. in 1994. In 1996, he arrived in Basle as a Research Associate. At the beginning of 2000, he was awarded a fellowship by the Swiss National Science Foundation with the position of Assistant Professor at Basle University. There he is conducting interdisciplinary research in the field of physico-organic chemistry.

“Measure the speed of supramolecular machines and learn to control it.”

molecular chemistry. "We are trying to determine at what speed dissociation and association between the two components takes place," continues Nau. "The speed may directly be related to the drug release rate."

Presently, the Basle group is using the fluorescent detector as the guest molecule and is studying the rate at which it binds to a host molecule. "We are trying to understand the factors which influence supramolecular kinetic processes. Additionally, with our detectors, we are also able to obtain fundamental information on the inside of a host molecule, a region which has been inaccessible until now. Later, we expect to use the detector as a marker grafted onto other guest molecules. Then it will be possible to study entire supramolecular machines."

### Biological processes

The Basle group is extending its methodology to the study of specific biological processes; this is the second type of system being investigated. "This extension is justified as much of the research in supramolecular chemistry is directed to the creation of functional machines in imitation of biological systems," reports Nau. "For example, we are studying diffusion kinetics in the cell membrane, kinetics which relate directly to its function. This work is very important for the development of synthetic membranes."

### Fundamental research

"Supramolecular kinetics is part of fundamental research," concludes Nau. "There is no doubt that industry will soon be involved with this field. We often discover possible applications during our work and we then look for contacts. This is what happened with our detectors and our analysis process for measuring vitamins E and C in cell membranes, which we have been able to commercialise." ■

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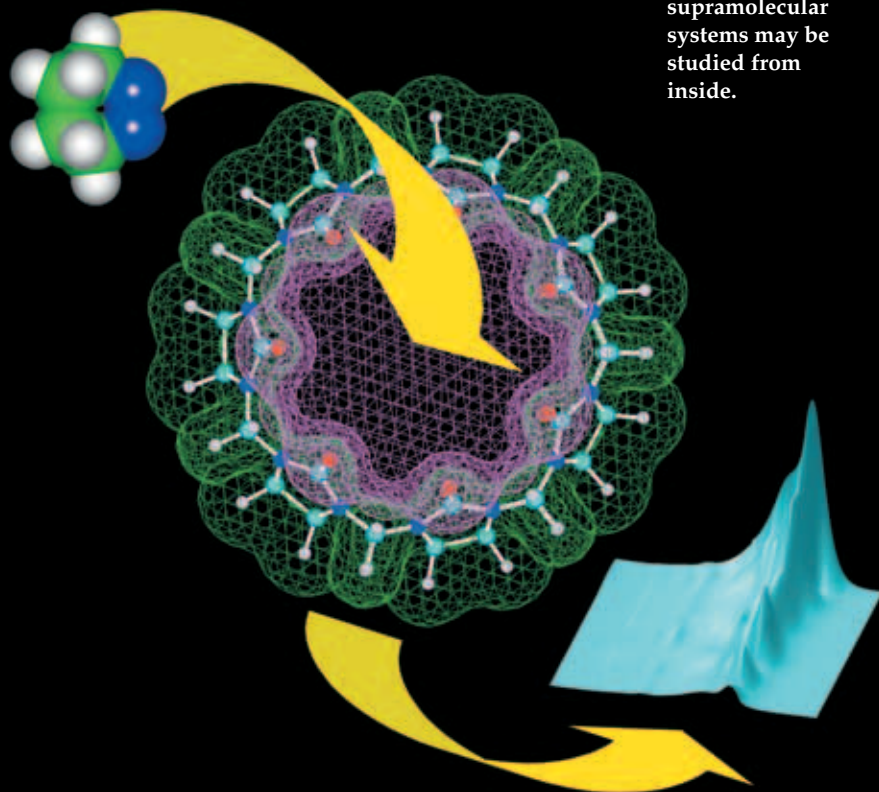
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**Module III:**  
Sensors and diagnostic tools

Using a fluorescent detector,  
supramolecular  
systems may be  
studied from  
inside.



“The creation of surface macromolecular docking sites  
by means of self-assembly”

# A surface for collecting

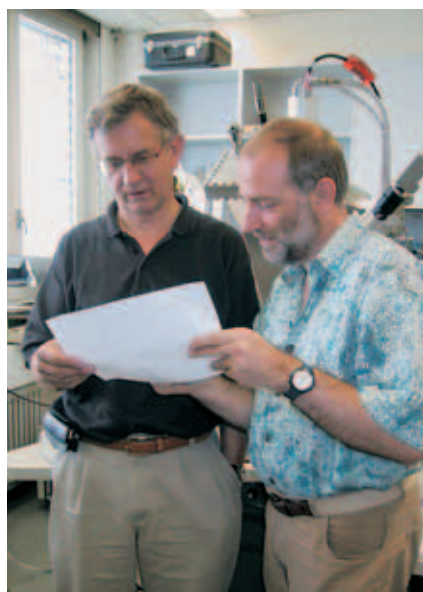
At the Laboratory for Surface Science and Technology of the Swiss Federal Institute of Technology Zurich (ETHZ), Professor Nicholas D. Spencer, Professor Jeffrey A. Hubbell and Doctor Marcus Textor hatched the idea of developing a new method for analyzing proteins. The basis of the idea is a surface to which macromolecules adhere selectively while retaining their activity.

Proteins are the most abundant molecules in living beings. They are responsible for the majority of cell activities and are also the main building blocks for cellular and extracellular structures. “It is fundamental to be able to observe these macromolecules which are only a few nanometres in size,” explains Spencer. “All the more so as the function of the molecules depends greatly on their structure.”

## Leave the macromolecules in their natural environment

Today, it is possible to determine the structure of proteins, thanks to progress in the fields of crystallography and microscopy. “However, a prerequisite for this technique is that the molecule to be observed exists in crystalline form. This condition is not easy to obtain on the one hand, and on the other the macromolecule is then extracted from its natural environment.”

Field of application: Bioanalytics.



“It is fundamental to be able to observe the structure of proteins on surfaces.”

The Zurich team’s objective is to solve this problem and its quest is for a method relying on the bonding of antibodies to analyse proteins. “The idea is to produce a surface to which these macromolecules bind selectively,” explains Spencer. “The conditions have to be as close to the natural environment as possible. Using Optical Waveguide Lightmode Spectroscopy (OWLS), a laser beam successively scans the surface and provides a highly-sensitive quantitative analysis.”

## How can the denaturation problem be solved?

The concept is clear but realising it remains a challenge. “The protein should not be able to bind anywhere and anyhow to the surface,” continues Textor. “If it does so, then its own structure would be modified – we call this denaturation – and it would thus lose its biological activity. Therefore, the surface must be able to repel proteins, but it should have equidistant docking sites which will accept macromolecules.”

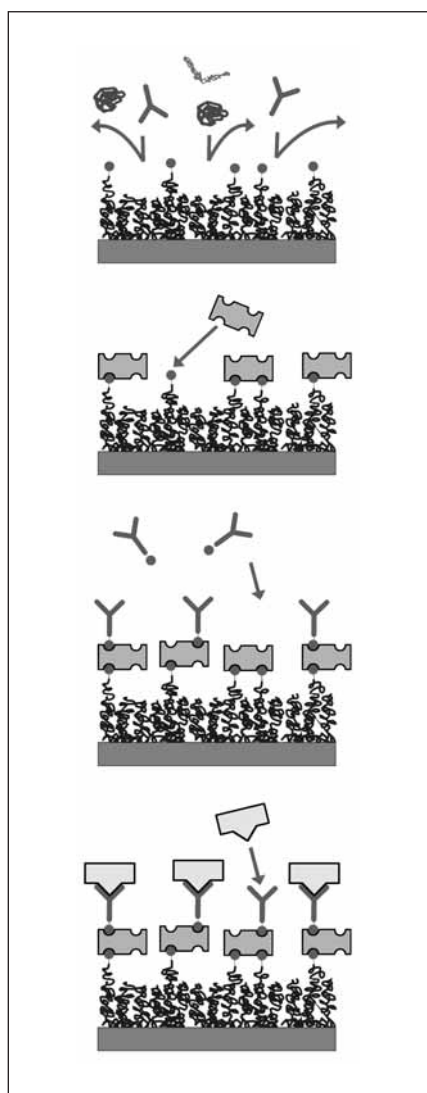
### Nicholas D. Spencer (right)

Born in 1955 in Bromley, England. He studied chemistry at Cambridge University. In 1980, he obtained his Ph.D. there with a thesis dealing with chemistry on the surface of gold and silver. Between 1982 and 1993, he worked as a researcher for the American firm Grace. In August 1993, he was appointed Professor for Surface Technology at the Materials Department of the ETH Zurich.

### Marcus Textor

Born in Wädenswil (ZH) in 1946. He completed his studies in chemistry at Zurich University. Again in Zurich, he obtained his Ph.D. for a thesis on organometallic chemistry. From 1978 to 1994, he worked with Alusuisse where in 1992, he was appointed Director of the Materials Department. Since 1994, he has worked at the ETH Zurich where he leads the group “Biomaterials and Surface Biosensors”.

# and studying proteins



The new surface macromolecular sensor developed at ETH Zurich is suited for highly-sensitive, highly selective detection of proteins.

The problem of denaturation is one of the most important problems encountered by a researcher wishing to capture a protein on a surface while retaining its functionality. "On the one hand," resumes Spencer, "a biomolecule in its natural conformation state has to be fixed to a docking site much smaller than itself so that the attachment itself exercises as little influence as possible. On the other hand, the interaction between the two components has to be strong enough to hold the protein on the surface."

### Create the surface

Another aspect of the problem: How can a surface be created which meets all these requirements? In one of the approaches tested, the Zurich team developed a polymer which offers no grip for proteins and can be deposited on an oxide surface. In the next phase it is possible to graft a functional group onto this polymer to be used as a docking site. "This is as if one and the same molecule were in two different states, one permitting anchoring of a protein, the other preventing it," explains Spencer.

Adsorption of the polymer on a surface is not instantaneous. It depends on the exposure time and on the concentration. By modifying these parameters, adds Textor, "islands of polymers ready to accommodate proteins may be generated." The same surface is then exposed much longer to the polymer without any docking site and it then occupies the remaining space. "We are now able to obtain a surface on which certain areas allow proteins to be deposited and others do not. However, we are still unable

**Module III:**  
Sensors and diagnostic tools

to control their distribution at the molecular scale."

In the medium term, many applications in the fields of biosensors and bioanalytics may benefit from the results of this research. "Competition is fierce. Spatial localization of docking sites in a non-interactive environment is, however, a unique approach," conclude both researchers with pride. ■

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# Deciphering the language of the cells

**G proteins and their related membrane receptors form one of the fundamental systems for cellular communication. Although they are the preferred target for a large number of drugs because of this, how they function at the molecular level has rarely been investigated. Horst Vogel, Professor at the Laboratory of Physical Chemistry of Polymers and Membranes of the Swiss Federal Institute of Technology Lausanne (EPFL), and Susanna Cotecchia, Professor at the University of Lausanne, hope to remedy this situation.**

**F**or cells of living organisms to be able to fulfil their function properly, they have to be able to communicate with their environment. To do this, they have receptors incorporated in the cell membrane. The family of the G protein-coupled receptors (GPCRs) is one of these receptor molecules. Their biological function consists of recognising a signal coming from the outside world and transmitting it to the inside of the cell via the G proteins with which they are coupled.

## The target for drugs

“These GPCRs form one of the most important families of receptor molecules,” explains Vogel. “Logically, they are the target of numerous pharmaceutical compounds. A large propor-

tion of currently used drugs is directed toward these membrane receptors and it is expected that this proportion will increase in the future.”

Paradoxically, much about these receptors remains obscure. Their structure as well as the exact mechanism of signal transfer at molecular level is not known in the large majority of cases. “The structure of only one GPCR has been specifically determined,” continues Vogel. This is rhodopsin, the visual receptor for retinal cells. However, this is not the only one. There are others which play a central role in the transmission of nerve signals, in the organs of taste and smell, etc.

## Light as a source of information

“In collaboration with Susanna Cotecchia, Full Professor at the Institute for Pharmacology of the University of Lausanne, we wish to develop a fast, reliable method allowing us to study signal transfer between the G protein and its receptor.” The method is based on fluorescence spectroscopy. Using this technique, fluorescent markers, small light-emitting molecules, are grafted onto membrane receptors. The light emitted provides a large amount of information for the researchers as it is very sensitive to the environment. “We gain information on the molecular structure of the receptors, on their ligand-binding properties, and finally on resulting structural change, which is directly related to signal transfer toward the G protein and to the intracellular signal amplification system.”

In comparison with more traditional techniques for investigating the structure of proteins, such as X-ray diffraction or nuclear magnetic resonance,



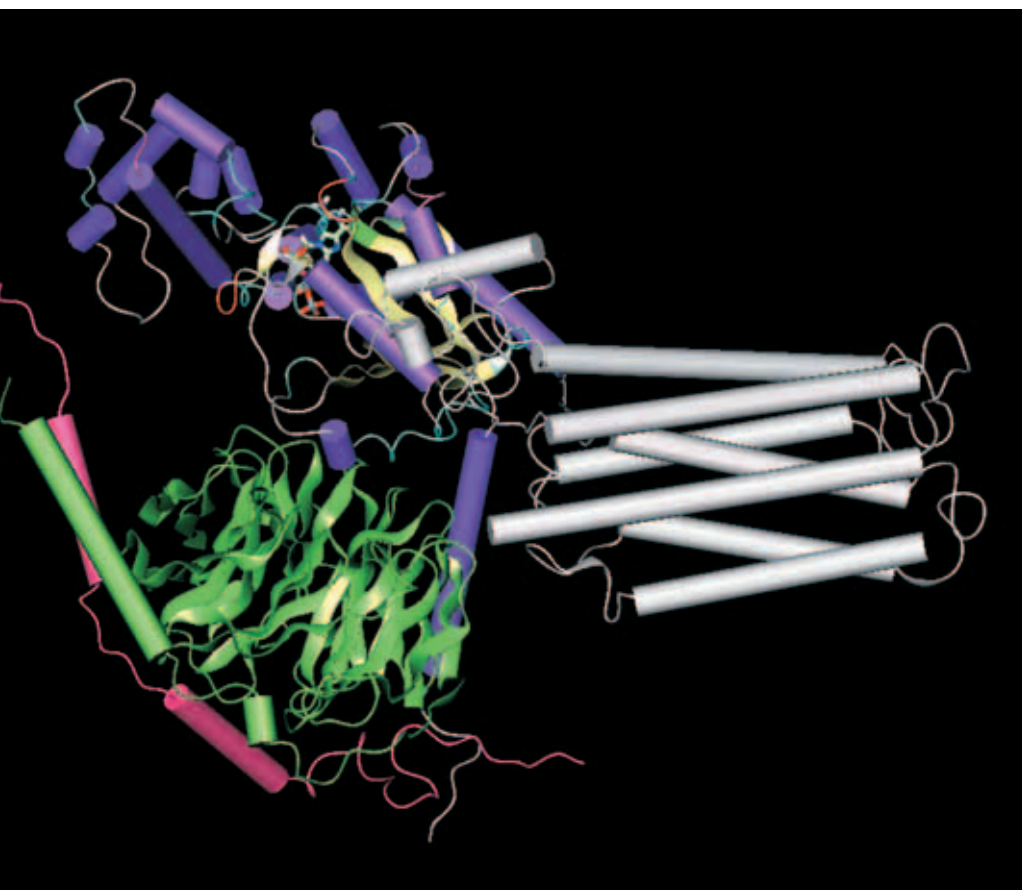
## Horst Vogel

Born in 1948 in Würzburg, Germany. After chemistry studies at Würzburg University, in 1978 he obtained his Ph.D. at the Max-Planck Institute for Biophysical Chemistry at Göttingen for thesis work on the structure of lipid membranes. He then worked with several research institutes such as the Max-Planck Institute for Biology at Tübingen, the Biozentrum in Basle, and the Karolinska Institute in Stockholm. In 1994, he was appointed Professor at the EPFL where he leads the Laboratory for Polymer and Membrane Physical Chemistry. His research work deals with the structure and the dynamics of membrane receptors as well as with bioanalytics, nano-biotechnology and the physical chemistry of interfaces.

Fields of application: Pharmacology, bioanalytics.

*“In this field, the path between fundamental research and application is very short.”*

Three-dimensional structural model of a receptor and its G protein.



fluorescence spectroscopy can be used under physiological conditions, for example in order to study a single living cell or cell fragments. “This permits us to work with very small amounts, even down to a single molecule. Through the analysis we gain instant information about receptor functions and are able to study a large number of receptors and active substances parallel to this.”

#### **Applications which are not so far off**

This approach is very fundamental. “However, it requires development of a new method and new concepts of analysis which may in a further phase lead to development of diagnostic instruments. The pharmaceutical industry is waiting for these in order to develop new therapeutic compounds. But this is still very much in the distant future.”

Whether from the point of view of fundamental research or application development, many research groups are interested in these G proteins and in their receptors. “All the large pharmaceutical companies are investigating these systems. There is also considerable interest in academic circles. There are not many methods available which permit researchers to work directly on the structure and functions of receptors under physiological conditions. This is where our approach is original and this is certainly our greatest advantage,” concludes Vogel. ■

**Module III:**  
Sensors and diagnostic tools

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# The smallest individual magnets

Magnetic properties of single molecules might be important in future in materials used for information storage. Professor Hans-Ulrich Güdel's research group at the University of Berne synthesises such structures and analyses their magnetic behaviour. During the first 18 months of the research project, various new structures could be synthesised and an important fundamental contribution was made to understanding the magnetic behaviour of molecules.

In the laboratories of Hans-Ulrich Güdel, Professor for Inorganic and Physical Chemistry at the University of Berne, an enormous number of test tubes containing green or red-brown solutions are to be found. “Green is the typical colour of nickel solutions and red-brown that of manganese,” explains Güdel. Within the scope of NRP 47, his research group synthesises nanoscale molecular magnets and studies their magnetic properties. These are structures with several metal ions incorporated into a skeleton of ligands which act as bridg-

ing agents holding the entire structure together.

These so-called “spin-clusters” represent a new class of inorganic compounds and they have specific magnetic properties. One of these days, molecular magnets may be implemented as materials for information storage. “There is still a lot of basic research that needs to be carried out to evaluate this potential in general. However, we know that new materials will be required for progressive miniaturisation of processors and memory units. The buzz word ‘quantum computing’ refers to new technologies relying on quantum phenomena. For example, our one-molecule magnets are so small that quantum tunnel effects may actually take place.” For the Bernese research group, the project contains two challenges in particular: synthesis of stable clusters and study of their magnetic properties.

“Our most important method is inelastic neutron scattering.”



## Hans-Ulrich Güdel

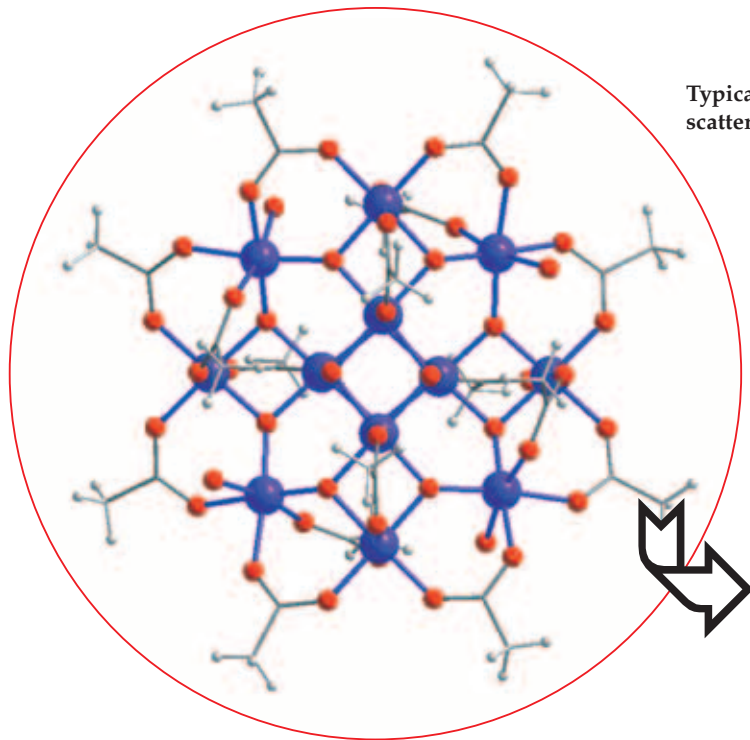
Studied chemistry in Berne, subsequent post-doctoral stays in Copenhagen and Canberra. Since 1978, he has been Professor in Berne. He has twice spent sabbaticals in California. Research themes in the field of chemistry and physics mainly focussed on material sciences, for example new types of photo-emission processes in inorganic materials with potential for application as luminophores for display screens, illumination, laser materials and scintillators. In addition, investigation of the magnetic properties of so-called “spin-clusters” and “individual molecular magnets” with application potential in information storage.

## International collaboration

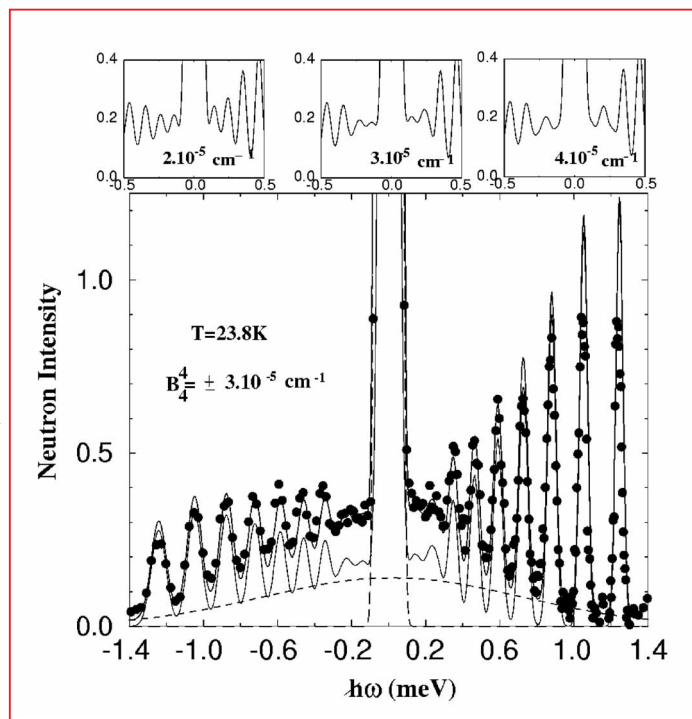
Measurements of magnetic properties are carried out at temperatures near absolute zero. Part of the analysis is carried out at 1.5 Kelvin in the modern magnetometer belonging to the Institute. “Our most important method, however, is inelastic neutron scattering. Here, the neutrons transfer part of their energy to the molecule being studied. We obtain information on the elementary magnetic excitations of our molecules from the energy difference,” explains Güdel. “At the Paul Scherrer Institute (PSI) we have access to a device called a spallation neutron source; in this device neutrons are formed by a proton beam colliding with target material rather than by nuclear reac-

Field of application:  
Information storage.





Typical spectrum for inelastic neutron scattering on manganese12 acetate.



tions.” However, measurements are also made at the Institut Laue-Langevin in Grenoble, at the Hahn-Meitner Institute in Berlin or at the Rutherford Lab in England. Because time for measurement periods at these high calibre institutes is only made available very selectively, this international collaboration is evidence of the quality of the Bernese research project. Additional project partners are research groups in Germany, Spain, France, England and the USA.

### Highlights from the first 18 months

“Within the first 10 months of the NRP 47 programme, we were able to prepare a spin-cluster with 7, 8 and 21 Ni<sup>2+</sup> ions by using a citrate as a ligand. We needed molecules with several metal ions and high total spin. The goal is to increase the temperature, thus suppressing quantum tunnel effects.” The second highlight concerns the field of physics. A research partner, George Christou’s group from Florida, made various clusters with manganese (Mn<sup>3+</sup>/Mn<sup>4+</sup>) ions and different ligands for neutron scattering, available to the Bernese. “We could

demonstrate the mechanism upon which the correlation between the chemical structure and magnetic properties is based. We were able to make this result directly available to theoretical physicists and thus improve understanding of magnetic behaviour in general. By probing further into such mechanisms we are laying the foundation for further research,” states Güdel happily.

In his opinion interdisciplinary collaboration is one of his success factors. “The fact that physicists and synthetic chemists tackle problems together has advanced research in our field. Indeed, we are still deep in the fundamental stage of research and far from any practical application, but the introduction of trans-disciplinary components increases the probability of a breakthrough.” ■

### Module IV: Molecular magnets

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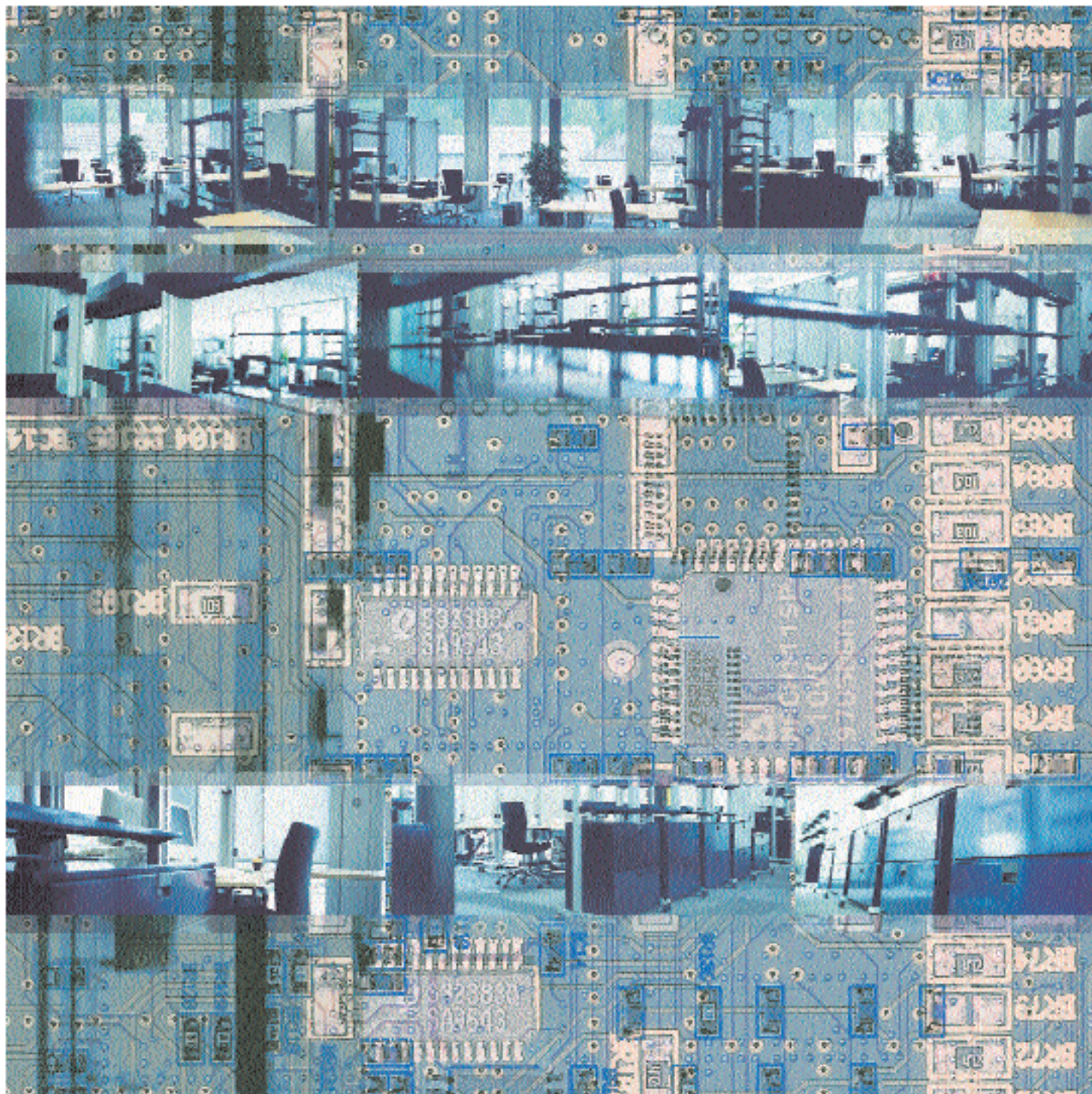
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NRP 47 has a trilingual Internet site in French, German and English. The site provides news and information about the programme and supra-molecular sciences to researchers and to all interested in the subject.



Work Structures

Work Processes

Work Flow

Work Spaces

Work Visions

eleven22

## Work Processes

Changing markets and technological developments are demanding widespread changes in organisational structures, ways of working and in work processes. eleven22, the flexible office system from USM, is designed to take these changes in its stride. Further information can be found at [www.eleven22.com](http://www.eleven22.com)