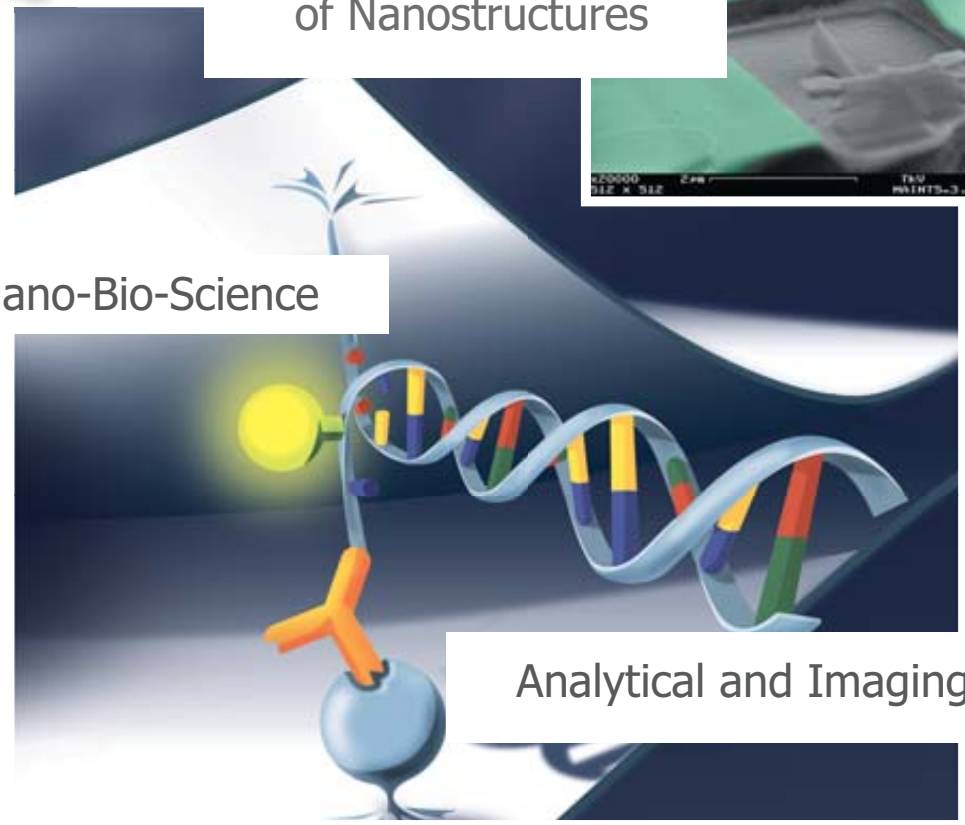
# Annual Report 2003

Chemical Assembly
of Nanostructures

Physical Properties
of Nanostructures

Nano-Bio-Science



Analytical and Imaging Methods

CeNS
Center for NanoScience
Ludwig-Maximilians-Universität

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*Research Fields of CeNS:*



*Other Activities in 2003*



*For futher information about CeNS and the web-based version of this report please visit our website: www.cens.de*

# *Introduction*

In the year 2003, CeNS continued to thrive successfully with new members, stimulating educational activities and impressive science.

We are pleased to welcome Prof. Bianca Hermann and Prof. Roland Kersting, recently appointed as associate professors at the Department of Physics of LMU and Prof. Patrick Cramer, full professor at the Department of Chemistry und Pharmacy of LMU, as new full CeNS members. We are also happy to welcome a large number of new extraordinary members, namely from the LMU the junior scientists Dr. Ulrich Gerland, Dr. Ferdinand Jamitzky, Dr. Don C. Lamb, Dr. Elizabeth Lupton, Dr. André Kempe, Dr. Jens Michaelis, Dr. Robert Stark, and the guest researcher Dr. Eduardo Mendoza, from the Max-Planck-Institute for Biochemistry the junior scientist Dr. Rainer Hillenbrand, and from the CeNS spin-off company attocube systems AG the CEO Dr. Dirk Haft. We also welcome Dr. Eva Natzer both as new scientific manager since April 2003 and extraordinary member of CeNS and extend many thanks to her predecessor Dr. Monika Kaempfe for her successful two years as CeNS manager wishing her success and joy in her new job.

Three members of CeNS have been offered attractive faculty positions elsewhere and have left or are in the process of leaving LMU to join other institutions but all plan to continue their fruitful cooperation within CeNS: Prof. Michael Reichling, as full professor at the University of Osnabrück and Prof. Matthias Rief as full professor of the Technical University of Munich and Professor Wilhelm Zwerger as full professor at the University of Innsbruck.

The continuous interdisciplinary research activities have been stimulated by the various CeNS workshops and seminars listed below, which hosted prominent guest speakers from all areas of NanoScience and introduced new students, postdocs, faculty members and industrial scientists to the network of CeNS.

- “Osaka University - EU - LMU Forum 2003 on Nanoscience and Nanotechnology”, January 16 - 17, 2003
- CeNS Winterschool 2003 “Current Issues of Nano-Bio-Science” in Mauterndorf (February 23 - 28, 2003)
- “CeNS meets Industry”, June 27, 2003
- CeNS Workshop at Kloster Seeon (September 28 - 30, 2003) “Transport in nanosystems”
- The weekly CeNS seminars

In addition to the above mentioned workshops the weekly “CeNS Oberseminar”, featured many highlight topics with prominent speakers and was accompanied by a large number of additional seminars given by visiting scientists on focused themes. These seminars form the weekly CeNS calendar (www.cens.de/calendar) and reflect the stimulating international interactions of CeNS. In addition CeNS hosted a large number of senior and junior guest researchers from all over the world who interacted fruitfully with CeNS members and students.

Triggered by the state visit of a Bavarian delegation headed by prime minister Dr. Edmund Stoiber to Quebec in May of 2003 CeNS started to form new international ties with NanoQuebec (www.nanoquebec.ca). CeNS also hosted a number of visiting

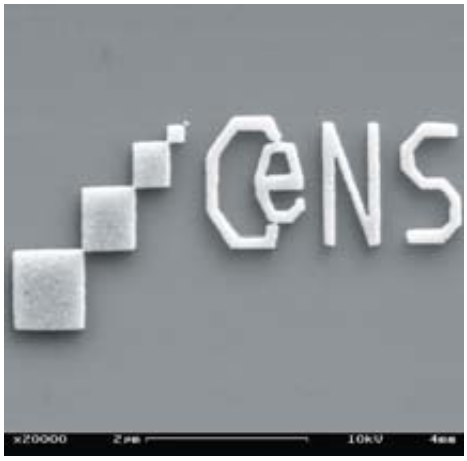
delegations e.g. from Japan and Canada as well as single company representatives who were interested in learning both about the wide spectrum of scientific activities at CeNS as well as its unorthodox and successfully operating structures based primarily on the voluntary engagement of CeNS members and associates. All these events contributed to an excellent international exchange and thus stimulated successfully the cooperative educational and research activities at CeNS in key areas of NanoScience and BioScience

The successful interdisciplinary research activities at CeNS are again best demonstrated by the many master (21) and doctoral (10) thesis projects completed in 2003 as well as by the large number of publications in international journals of high visibility, many of which are coauthored by CeNS members belonging to different groups and disciplines as well as external partners. Consequently a large number of invited talks at conferences and workshops have been extended to CeNS members and associates and many of its scientific achievements have received special mention in the media. A significant number of joint publications can be traced to informal encounters between CeNS members at previous workshops.

The CeNS philosophy to operate as a voluntary network of enthusiastic researchers sharing their know-how and facilities while avoiding a colossal institutional structure continues to prove very successful. The informal and flexible operation of CeNS guided by a minimal organizational team strengthens in particular the role of junior scientists who are spearheading research and innovation. We thank our University and the State of Bavaria for supporting our initiative and hope they will continue to trust the CeNS concept with its special spirit and culture that has found worldwide recognition.

Hoping that our friends and colleagues all over the world will enjoy the more detailed report below it is my pleasure to thank all CeNS members and associates for contributing to excellent science, promising technologies and valuable and joyful education.

Jörg P. Kotthaus
Spokesman of the board



*Organosilicates as insulating layers on planar GaAs substrates and CdSe-nanocrystals for biological applications*

The aim of this project, carried out by Christian Kirchner, Markus Seitz, Wolfgang Parak and Hermann Gaub is to realize a sensitive semiconductor device to directly measure cellular processes (metabolism, neuronal activity) in adherent cells.

Introducing arsen or cadmium based semiconductor material to biological systems, it is important to use highly efficient insulating barriers to avoid toxication. For the use on a planar GaAs based biosensor (FAPS), we put organosilicate layers of cross-linked mercaptopropyltrimethoxysilan on GaAs surfaces. The potential ability of that system to electrically passivate the semiconductors surface motivated us to do microstructural investigations of the GaAs-organosilicate interface by measurements of X-ray reflectivity under grazing incidence.

Similar organosilicate layers are currently applied to CdSe based nanocrystals, for their later use as long-term fluorescence labels for living cells. Beyond other encapsulation methods, we do a systematical study to compare the efficiency of the protecting layers and to find the toxic concentration limits of the insulated particles in cell cultures.

*Physical Properties of Polymers*

Surface grafted polymer brushes were characterized by single molecular force spectroscopy in the group of Hermann Gaub and Markus Seitz. The technique was also used to perform single molecule desorptions of polyelectrolyte chains from metal surfaces and to electrochemically manipulate desorption forces.

*Physical approaches to Biotechnology and the Origin of Life*

Thermophoresis - the movement of molecules by temperature gradients - is a strong effect for DNA and biomolecules of comparable size. This finding has unexpected consequences for applications in microfluidic biotechnology. In the groups of Hermann Gaub and Dieter Braun, it is planned to study the following, experimentally tightly connected questions:

- measure and understand thermophoresis of DNA and proteins in complex liquids,
- thermophoretically separate and accumulate DNA/proteins in microfluidic settings,
- create a microscopic Clusius accumulation tube for DNA,
- synthesize biopolymers by fast cooling in a convection,
- explore DNA hairpin kinetics upon fast cooling to optimize DNA detection
- study the speed limitations of convective PCR.

In all of the experiments, temperature gradients are the driving force. They thus tackle simultaneously the hypothesis formulated on the origin of life: are temperature gradients sufficient to polymer-

ize, accumulate and replicate the first living biopolymers in porous stones near hydrothermal vents?

*Cell to cell adhesion and Interaction between DNA and Proteins*
In the group of Hermann Gaub and Martin Benoit, adhesion forces down to the single molecular level between individual cells are measured. Adhesion molecules and molecular arrangements on the cells are characterized as well as signaling and other cellular processes effecting the adhesion of cells.
Cells have developed various strategies to avoid or repair damage of the DNA. The SOS system of E.coli is coordinated by two proteins: LexA, a repressor protein of a number of unlinked genes, and the co-protease RecA. As known to date LexA controls 31 genes with slightly different DNA binding motifs allowing a variable degree of repression from one gene to the other. Hermann Gaub and Ferdinand Kühner employed AFM-based single molecule force spectroscopy to characterize the interaction of LexA protein with two different DNA motifs: recA and yebG.

*Force spectroscopy on metallo-supramolecular systems:*
The investigation of metallo-supramolecular complexes on the molecular level using single-molecule force spectroscopy allowed the detailed investigation of terpyridine-ruthenium metal complexes in the group of Ulrich Schubert. The rupture force of an individual complex was found to be of an ideal value for their future use in functional nanomaterials (cooperation with Hermann Gaub).

*Structural and Physical Properties of Proteins*
Force is a structural control parameter that is important in many biologically relevant systems. One focus of the group of Matthias Rief is the self-organization and folding of protein structures. The group is investigating the folding and unfolding pathways of individual protein domains, the mechanics of cytoskeletal proteins as well as of muscle proteins. The group of Matthias Rief is collaborating with Roland Netz and Hermann Gaub to understand the mechanical processes that determine biopolymer elasticity in the limit of very high stretching forces above 1 nN.
Furthermore, the chemo-mechanical coupling of molecular motors and the motor proteins myosin V and kinesin are investigated in single molecule mechanical and optical experiments.

*Manipulation of DNA on solid surfaces*
Fluorescence microscopy allows the direct observation of individual biological macromolecules. The Rädler group studies linear DNA molecules electrostatically adsorbed to cationic substrate-supported lipid bilayers. The goal of the project is to manipulate DNA by structured solid surfaces. For example groves edged into silicon substrates lead to parallel alignment of DNA by competition of bending and electrostatic forces. These "directed polymers" in external elastic fields are expected to exhibited novel statistical behaviour.

*Simultaneous AFM manipulation and optical imaging of single DNA molecules*

During the last decade, optical and atomic force spectroscopy have independently been developed as techniques for the investigation of single molecules. Since the observation of only one molecule at a time avoids averaging and thus removes the need for external synchronization commonly needed in bulk spectroscopy, both techniques have revealed a wealth of hitherto unavailable information. During the last year, first experiments which combine both techniques were developed in the groups of Christoph Bräuchle and Andreas Zumbusch and have been applied in studies of single fluorescently labelled DNA molecules on transparent surfaces. On one hand, these experiments give new insight in the binding of DNA to hydrophobic and polar surfaces. The results show ways, how DNA can be used to fabricate stable micrometer sized structures with DNA on such surfaces in a controlled manner. On the other hand, the setup was used to perform a new type of lateral force spectroscopy, by horizontally stretching a single DNA strand and for the first time the visualization of the rupture of polymer was made possible.

*Single molecule and bulk experiments of the photophysical properties of the Green Fluorescent Protein (GFP)*

In the past ten years, the family of the auto fluorescent proteins became the most important labels in molecular biology. A detailed knowledge of their photo physics is still prerequisite for expanding the applications to modern fluorescence microscopy techniques like fluorescence lifetime imaging, single molecule imaging and resolution improvement by STED (stimulated emission depletion) microscopy. The current focus of research in this field is the unravelling of the influence of point mutations on the photo physical properties of the GFP. For this purpose, comparative experiments with a variety of mutants of the GFP are performed in the groups of Christoph Bräuchle and Andreas Zumbusch. The results of these experiments allowed to stabilize an intermediate form of the GFP's photo cycle. In this concern, the introduction of artificial amino acids in the proteins' primary structure is of special importance as a new approach for tuning the fluorescence properties. In a collaboration with the group of Nediljko Budisa, MPI for Biochemistry, the imaging capabilities of the gold fluorescent protein, a newly designed protein with a large Stokes-shift, were demonstrated. Further experiments are expected to give insights in the bleaching behaviour of fluorescent proteins.

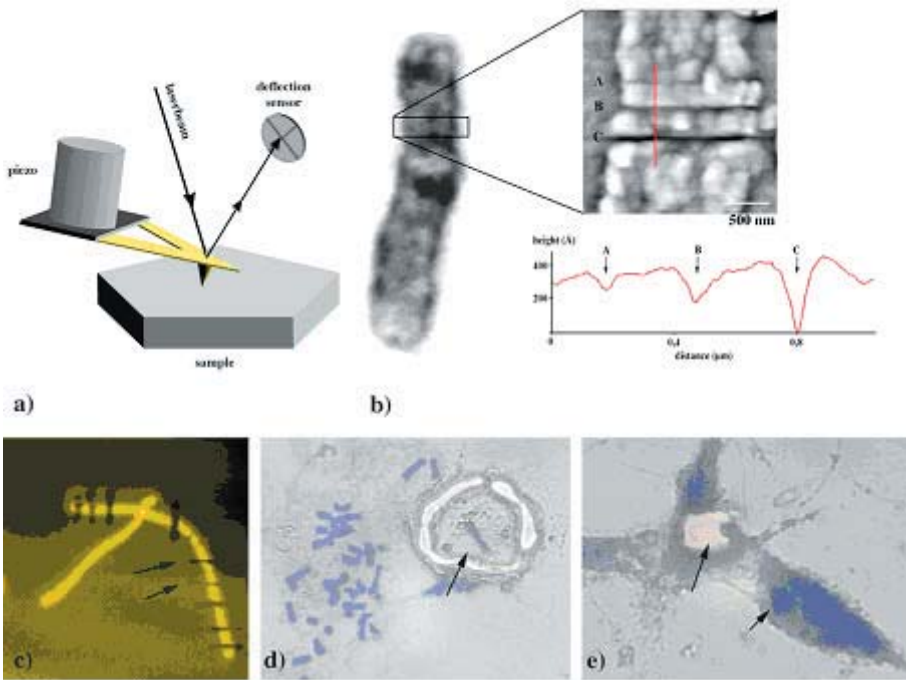
*Single Molecule Spectroscopy of the Phycoerythrocyanin (PEC)*

Phycoerythrocyanin (PEC) is the short wavelength absorbing pigment in the light harvesting complex of cyanobacteria. The group of Andreas Zumbusch performs single molecule investigations of PEC at room temperature as well as at cryogenic temperatures in order to gain a better understanding of the energy transfer processes in PEC in a collaboration with the group of Hugo Scheer (Botanisches Institut, LMU Munich). The different subunits are investigated sepa-

rately and the influence of aggregation of the different subunits constituting the native trimeric and hexameric form of the protein are studied. Results from experiments employing polarization sensitive and spectrally selective excitation and emission detection show a wealth of different behaviours unobservable with common bulk techniques.

*Manipulation and Extraction of DNA*

Nano- and micromechanical manipulation and extraction of genetic material play an important role in the development of patient based diagnostics. In the group of Wolfgang Heckl and Stefan Thalhammer, it is possible to isolate femtogram of DNA from any related genetic region by using down scaling approaches like atomic force microscopy based microdissection and laser microisolation.




a) Setup of an Atomic Force Microscope (AFM), consisting of a piezo driven actuator and a laser beam deflection sensor; b) non-contact AFM image of a human metaphase chromosome after AFM microdissection (arrows indicate the microdissected regions with increasing loading forces, size around 100 nm); c) AFM image of laser microdissected chromosomal areas of a Muntjac muntiacus metaphase chromosome (see arrows, size around 350 nm); d) laser based isolation of a single metaphase chromosome (see arrow); e) laser based isolation of a single nucleus (see long arrow) (short arrow indicates a not isolated nucleus) (W. Heckl).

*The biological nanomachine RNA polymerase II*

Expression of the genetic information in living cells involves two major steps: RNA synthesis from a DNA template (transcription), and protein synthesis based on RNA (translation).

The group of Patrick Cramer is interested in the molecular mechanisms of gene transcription. X-ray crystallography is used to elucidate the three-dimensional structure of large and transient multiprotein complexes. In 2003, two major goals were achieved. First, the architecture of the complete enzyme responsible for gene transcription, RNA polymerase II, was determined. The enzyme comprises 12 polypeptide subunits and has a molecular weight of around 500.000 Dalton. Second, the structure of the first transient complex of RNA polymerase II with a transcription factor, a 13th polypeptide that binds to the enzyme surface and modulates function, was determined. These achievements strongly advanced the understanding of the mechanism of gene transcription and the structure of the underlying multiprotein machinery. The studies also led to the development and application of new techniques for structural studies of other very large macromolecular assemblies.

*Atomic Force Microscopy (AFM) of biological macromolecules*

The ability of the Atomic Force Microscope (AFM) to work very well in fluids. e.g. in buffer, makes the AFM an excellent tool for investigations of biological specimens. The main focus of the group of Reinhard Guckenberger is to investigate the functions of such macromolecular complexes which are involved in the folding and degradation of proteins. Proteins can only function correctly when they are in the correct folding state. Some proteins need the help of so called chaperonins to reach this state. Degradation of proteins is part of the functional cycle of cells (recycling of proteins) but is also important to remove incorrectly folded proteins (a kind of quality control).

To be more specific: The functional cycle of the chaperonin GroEL is investigated, which is driven by ATP, for various protein substrates to be folded. The experiments focused on the single ring mutant of GroEL.

The second biological project in the group of Reinhard Guckenberger is about the 20S proteasome which is responsible for the degradation of incorrectly folded proteins in archaea. After investigation of preparation methods to achieve homogeneous samples with defined orientation of the proteasomes, the group will now switch to functional studies.

*Nanodevices and bio-templated nanostructures*

Biophysical and bioinspired techniques are utilized in the group of Friedrich Simmel to create new electronic and mechanical functions in a bottom-up approach. To this end, the unique molecular recognition properties of DNA molecules are used to build complex supramolecular networks or to direct the synthesis of functional materials, but also to construct artificial molecular machines. As a means to direct self-assembly within microfabricated structures, the behavior of DNA molecules in electrical fields is studied in collaboration with the groups of Joachim Rädler and Roland Netz.

Another fruitful lab-on-a-chip oriented project has been continued with the young start-up Nanion in the area of improving patch-clamp techniques. Here single ion channel recordings have been successfully performed on a glass chip developed in cooperation with the Kotthaus group. In collaboration with the group of Friedrich Simmel, Nanion's on-chip approach is now combined with high-frequency techniques from which additional information on the switching behavior of ion channel proteins is expected.

*Water-structuring at interfaces*

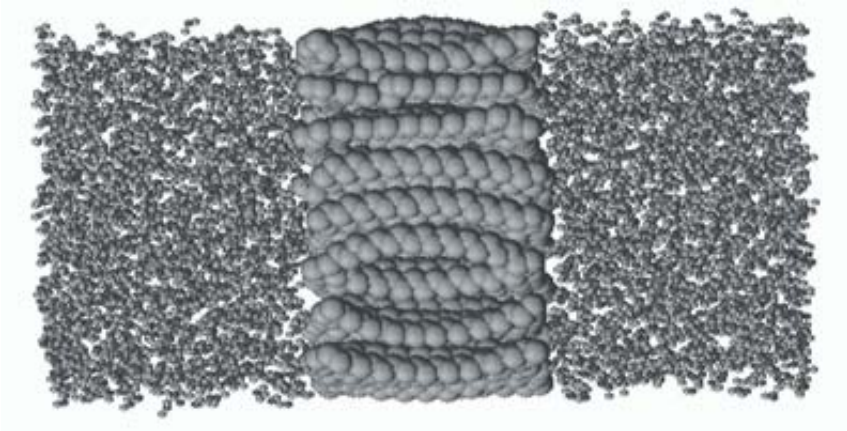
The group of Roland Netz, in close collaboration with the group of Hermann Gaub, focuses on the theoretical understanding of nano-structures formed from soft objects such as membranes, polymers and proteins. The methodology ranges from Molecular-Dynamics simulations, Stokesian Dynamics simulations, over ab-initio quantum-chemistry calculations to field-theoretic techniques.

For hydrophobic substrates in contact with water, it is known since a long time that the water density is reduced at the hydrophobic surface. It seems fair to say that without a proper characterization of the behavior of water at hydrophobic surfaces, no true understanding of the properties of such surfaces and their interactions will be possible.

Quite possibly, many of the features interpreted as being inherent to surfaces themselves, might in fact reflect properties of the interfacial water layer instead (e.g. polymer-adsorption energies as they are studied in Gaub's group with the AFM). The water density profile is considered close to a planar surface using Molecular Dynamics (MD) simulations. At room temperature and normal pressure, we obtain for the depletion thickness of a planar hydrophobic substrate the value d = 2.565 Angstrom, which is of the order of the length obtained in recent neutron scattering experiments by Grunze and Findenegg.

What do these results mean for Nano-surfaces? Many of the surfaces used in experiments are in fact, if one forgets about the charged groups for a moment, of hydrophobic nature. A layer of reduced water density at such surfaces means that the effective dielectric constant is reduced, which in turn means that the association-dissociation equilibrium of surface charges and all other properties will

be perturbed. For interactions between surfaces it means that the hydrophobic attraction due to the overlap of the depletion layers might very well dominate the resulting behavior.



Snapshot of a MD simulation of a planar hydrophobic slab (made up of 64 alkane molecules) in contact with a water slab, consisting of 2781 SPC/E water molecules. Between the alkane slab and the water layer a region of reduced density appears. (R. Netz)

*Electronic properties of nanoscale systems*

The study of electronic properties of nanoscale systems is motivated by the increasing importance of quantum effects as electronic devices decrease in size and the limitations of scaling of traditional electronic devices such as the Metal-Oxide-Semiconductor Field-Effect-Transistor (MOSFET). The studies of quantum phenomena aim at finding new ways of information processing. One current major research theme are ways to implement and control quantum bits on the basis of solid state electronic and optical devices and thus lay the ground work for a future quantum information technology. In part this research is embedded in the SFB 631 — a long term research platform on "Solid-State Based Quantum Information Processing", funded by the German Science Foundation (DFG) since July 2003. Quantum dots defined electrostatically via surface gates in a GaAs-AlGaAs heterostructure are considered promising candidates for the implementation of quantum information registers, so-called qubits, in solids. Electron transport through nanostructures formed electrostatically on GaAs/AlGaAs heterostructures is studied at ultra-low temperatures in the group of Jörg Kotthaus jointly with Robert Blick and Stefan Ludwig. Using SEM lithography gate electrodes are deposited on the GaAs/AlGaAs crystal surface. By charging these gate electrodes, a potential landscape is generated, depleting parts of the two-dimensional electron gas and, hence, creating electronic tunnel barriers and conducting islands. Quantum dots, i.e.such small conducting islands, are promising candidates for so-called qubits, the elementary information registers in quantum information processing. The possibility of tuneable coupling of several such quantum dots, e.g. by forming double quantum dots in separately accessible circuits, provides one main motivation for ongoing research. Another important aspect is the prospect of real-time control of the electronic quantum states in such dots. The experimental effort profits from the continuous interactions with the group of Jan von Delft and Frank Wilhelm. They investigated the optimization of quantum logic gates as they can be implemented in superconducting nanocircuits and in semiconductor quantum dots. The main focus is to decouple from the hostile conditions for quantum coherence as they naturally occur in a solid-state environment. Quantum design rules for optimization strategies using symmetry, active refocusing, and nonequilibrium control were obtained. Furthermore, the group has analyzed far from equilibrium phenomena in superconducting nanostructures as they are used in ultrafast digital electronics.

As starting material for the realization of quantum dots excellent heterostructure wafers grown by molecular beam are graciously provided by several groups, in particular by those of Gerhard Abstreiter and Dieter Schuh, Walter-Schottky-Institut of the Technical University Munich,and Werner Wegscheider, Universität Regensburg.

In the group of Robert Blick and Jörg Kotthaus, quantum dots integrated in freely suspended phonon cavities were investigated. A nanobridge containing a two-dimensional electron system (2DES) was excavated from an AlGaAs/GaAs heterostructure by etching. The integrated 2DES can then be depleted further by applying a negative voltage to a nearby gate to form a quantum dot in the bridge. At low temperatures one observes in addition to single electron tunnelling and Coulomb-blockade the new phenomenon of phonon blockade, characteristic for such suspended phonon cavities. In a collaboration lead by Bert Lorenz and Robert Blick similar suspended nanowires were fabricated in highly n-doped silicon with lateral dimensions down to about 40 nm. Random dopant fluctuations in these wires lead to the formation of multiple tunnel junctions, utilized for Coulomb blockade thermometry. In the low bias regime, relaxation via discrete acoustic phonon modes was observed.

In suspended Si nanowires the group of Jörg Kotthaus studied the temperature dependence of Coulomb-blockade-induced conductance minima for their possible utilization as a primary electron thermometer. The wave nature of electron transport is reflected in characteristic conductance oscillations studied in very narrow Silicon field-effect controlled Si nanowires resulting from electron interference. Non-linear multi-mode ballistic electron transport through lateral nanowires has now been demonstrated to be responsible for the ballistic rectification observed in asymmetric mesoscopic four-terminal junctions on GaAs-AlGaAs heterostructures.
Alternatively to top-down fabricated semiconductor nanostructures there exist many efforts to use bottom-up assembled molecular structures for the study and possible utilization of electron transport in nanoscale systems. Presently, routes to combine top-down fabrication with self-assembly techniques aiming to create and investigate electronic devices out of individual carbon nanotubes as well as mesoscopic ensembles of self-assembled molecules are explored. Additional insight into mesoscopic transport phenomena is gained by the study of its dependence on in-situ tunable strain.

*NEMS*

In the nanometer regime electronic, mechanical and optical properties become often inseparably connected. Therefore in recent years the groups of Jörg Kotthaus and Bert Lorenz have increased their activities on studying Nano-Electro-Mechanical Systems, in short NEMS, ranging from fundamental studies of the resonant behavior of nanoscale bridges fabricated out of semiconductors to their development as sensing and actuating devices. A still unresolved problem is how to easily excite and control motion of nanomechanical elements. Ways to efficiently drive such nanoscale resonators by electric, magnetic, mechanic as well as optically induced forces are one current research aspect. Sensing the mechanical motion with nanometer resolution via capacitance, current or optical reflection is another basic theme of ongoing research.

In the group of Khaled Karrai experiments have been performed on tuning the mechanics of microlevers with light that open new routes for driving and controlling optically nanomechanical systems. They use a microcavity in which one of the mirrors is a soft compliant microlever optimized to detect bolometric forces. In this set-up the static compliance of the lever can either be decreased to zero or increased considerably depending on the detuning of the light with respect to the cavity resonance.
Alternatively nanoscale beams fabricated out of a GaAlAs heterostructure can be driven with surface acoustic waves utilizing parametric excitation, as was demonstrated at frequencies of around 400 MHz in a collaboration lead by Robert Blick and Achim Wixforth. Such acoustic excitation mechanism will allow the integration of nanomechanical systems in low cost, room temperature applications for information processing and sensors.
NEMS devices carved out of Silicon on insulator (SOI) are studied in the group of Jörg Kotthaus and Robert Blick with the aim of controlling the coupling between adjacent resonators, understanding and decreasing the damping mechanism as well as driving them more efficiently via Coulomb forces. The reduction of mechanical losses is crucial for excitation, since the attainable forces in NEMS are limited. Here a shuttle device in a tuning-fork configuration proofed a way to enhance the mechanical quality factor Q.
Electrostatic actuation of a nanoelectromechanical system aimed at making nano-tweezers can also be made visible via a newly developed optical detection method (collaboration of Bert Lorenz and Khaled Karrai). Images of the tweezers structures are taken by scanning confocal microscopy while the prongs are electrostatically actuated via a low frequency ac voltage. The images, which are demodulated at the actuation frequency and its higher harmonics, clearly resolve the actuating parts of the tweezers.

*Optical properties of single self-assembled quantum dots*
In the group of Khaled Karraï optical properties of single self-assembled quantum dots are investigated. Excitons in self-assembled quantum dots constitute another atomic-like solid-state system ideally suited to study quantum properties and attractive for storing qubits. The self-assembled InAs quantum dots are grown by molecular beam epitaxy in the group of Pierre Petroff in UC Santa Barbara. Together with the group of Richard Warburton (Heriot Watt University Edinburgh), know-how of filling quantum dots with well-defined exciton and electron occupation was combined with the expertise developed to perform a range of luminescence and absorption experiments on individual quantum dots. Electron-occupation dependent fine-structure of the luminescence nicely reflects the quantum nature of the charged excitonic states (see B. Urbaszek et al.) as well as their interaction with a nearby two-dimensional electron system. Absorption spectroscopy on individual quantum dots enabled by Stark-shift modulation spectroscopy yields quantitative insight lifetime broadening and oscillator strength of excitonic

transitions and charge-tunable exchange coupling (see B. Alèn et al.). In an international collaboration the experimental studies are complemented by theoretical efforts aiming to understand the interaction between excitons in the dot and a nearby Fermi sea. Such problems were investigated in the group of Khaled Karraï together with the theoretical input of Alexander Govorov. For instance it is predicted that charged excitons confined in a quantum dot can couple to a nearby two-dimensional electron system to form a Kondo exciton.

Inspired by recent experimental results from the group of Prof. Khaled Karrai on the photoluminescence of quantum dots whose localized states hybridise with the delocalised states of a nearby 2-dimensional electron gas, the group of Jan von Delft has used the numerical renormalization group to study the absorption lineshapes of such dots. In particular, it was shown that these lineshapes should bear strong signatures of Kondo correlations, for dots tuned into the Kondo regime.

*Opto-mechanics of microlevers*
Though still on a micromechanical scale the group of Khaled Karraï has performed experiments on tuning the mechanics of microlevers with light that open new routes for driving and controlling optically nano-mechanical systems. Such schemes are expected to be used soon with nanomechanical devices.

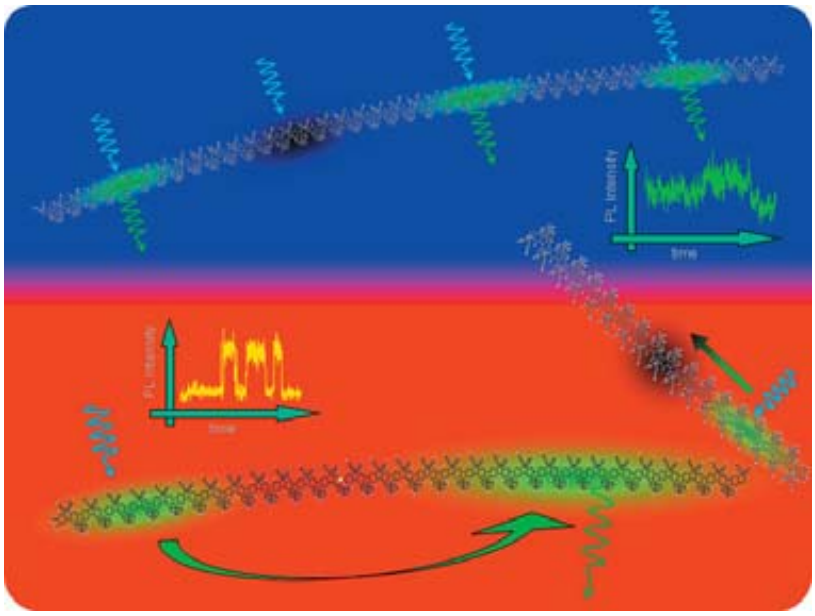
*Single Molecule Microscopy and Spectroscopy in Nanostructured Porous Materials*
The characterization of the static and dynamic behaviours of single molecules in the group of Christoph Bräuchle allows for a very thorough description of the molecule and its immediate surroundings. In this sense, the single molecules incorporated into the nanometer sized structures of molecular sieves, are used as probes to obtain a new wealth of information for these host-guest materials: The orientational distribution of molecules, the dynamic spectral, orientational and translational behaviour of individual molecules in molecular sieves, exemplify the possibility to characterize these materials in an unprecedented level of detail. The cooperation with the group of Thomas Bein, which has high expertise in the synthesis of nanoporous materials, proved to be very fruitful. It has been possible to characterize the diffusion of guest molecules in different molecular sieves synthesized by that group.

*Single molecule fluorescence spectroscopy of conjugated polymers*

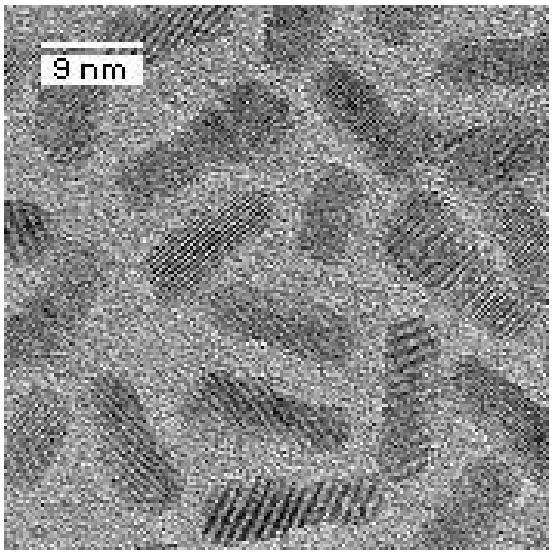
Plastic electronics relies on conjugated polymers - long molecular chains made up of interconnected segments called chromophores, which form the basic photoactive units. The interaction between chromophores on a chain defines the overall properties of the polymer molecule and is therefore very important to the performance of a material in an actual device. Little is known, however, about the strength and nature of this interaction. The Photonics and Optoelectronics Group with Thomas Klar, John Lupton, Andrey Rogach and Jochen Feldmann now succeeded in identifying the fluorescence arising from individual chromophore units constituting a polymer chain. The project was carried out in cooperation with Ullrich Scherf, University of Wuppertal. This enables a direct study of the interaction between these discrete building blocks. It was found that elementary photoexcitations migrate along the polymer chain from chromophore to chromophore, whereby the migration speed is controlled by the spectral properties of the chromophore units. At low temperatures these segments only communicate very weakly with each other and behave as independent sources of light. As the spectral width of the chromophores increases with rising temperature, they begin to talk to one another. The entire chain then acts as one single emitting state. The correlation we draw between the molecular electronic properties and the efficiency of energy transfer provides important input into material design for plastic electronic devices such as light-emitting diodes and solar cells. A high degree of mobility of excitation energy is desirable, for example, in solar cells, where it forms the basis for efficient light harvesting. In contrast, energy migration is detrimental in LEDs, where it leads to trapping and quenching in dark states. The new microscopic picture of energy transfer within a single molecule promises to deepen the understanding of polymeric semiconductors and guide the development of more efficient materials. In turn, the nanoscale control of energy transfer opens up new directions to single molecule optoelectronic devices.

*Highly emissive colloidal CdSe/CdS heterostructures*

For the groups of Thomas Klar, John Lupton, Andrey Rogach and Jochen Feldmann Semiconductor nanocrystals are of both practical and fundamental interest because their luminescent properties can be finely tuned by changing either the size or the shape of the particle, without needing to alter its composition. For example, rod-shaped particles show different emissive properties than spherical ones, because the electrons and holes are no longer equally confined in all three dimensions. It was shown that efficient shape control may be achieved in the shell of colloidally grown semiconductor nanocrystals (independent of the core) allowing the combination of a 0-D spherical CdSe core with a 1-D rod-like CdS shell. In these heterostructures, electrons delocalize across the entire nanoparticle, whereas holes are more strongly confined to the cores. These nanocrystals exhibit linearly polarised emission with a room temperature quantum efficiency above 70% and display large, length dependent Stokes shifts as well as extinction coefficients by over an order of magnitude larger with respect to bare CdSe cores.



Interactions of the individual light sources (chromophores) on a polymer chain. At low temperatures (blue) the elementary excitations of the chromophores are virtually immobile. In this case, a dark, non-emissive chromophore (black) cannot influence the emission from the other segments. At elevated temperatures (red) the molecular excitations become more mobile and migrate along the chain. A single dark segment on the chain leads to the extinction of the entire molecular fluorescence.




TEM image of CdSe/CdS nanorods (A. Rogach)

*Structural Investigations of DNA-peptide complexes*

The structure of DNA-peptide composite complexes was in the focus of synchrotron X-ray scattering experiments of the Rädler group. In particular DNA-polylysine complexes were studied and the phase behaviour as a function of salt compared with theoretical calculations from Roland Netz. One of the intriguing medical application of DNA complexes is to design molecular carriers that are able to efficiently deliver plasmid DNA, antisense DNA or interfering RNA as therapeutic agents. A rational design of synthetic gene transfer systems aims at mimicking natural viruses using self-organized DNA/lipid/polypeptide aggregates. This approach is pursued in a trias collaboration between E. Wagner at the pharmaceutical department, the Bräuchle group and the Rädler group, that cover synthesis, particle tracing and complex characterization respectively.

# Chemical assembly of nanostructures

*Chemically assembled nanostructures for chemical sensing*

The goal of this project is the development of a parallel platform for chemical sensing of vapor-phase analytes. The approach is based on position-sensitive surface-acoustic wave (SAW) sensors that are modified with arrays of chemoselective nanostructures. The SAW sensors are being developed by the Kotthaus and Wixforth groups and fabricated in part by the CeNS spin-off Advalytix AG. With the formation of the new group of Achim Wixforth at the university of Augsburg these activities are continuously shifted from Munich to Augsburg. Chemical gas sensors employing nanoporous films as selective absorbers are developed in the group of Thomas Bein in cooperation with the the spin-off company NanoScape (www.nanoscape.de). These receptors exhibit a different adsorption behavior for molecules having different sizes, thus being able to "sort" the molecules according to size. These nanoporous films areembedded into the SAW sensing the gas absorption via the modified propagation of SAW in a delay line. First sensor-chip prototypes demonstrate the desired molecular shape selectivity of the different porous films.

Additional assembly techniques used in the group of Thomas Bein range from oriented zeolite crystallization on self-assembled monolayers to the electrostatic assembly of pre-formed nanoscale zeolite crystals. Structural studies of these films are being pursued with H. Metzger at ILL at Grenoble, using synchrotron radiation.

In cooperation with Advalytix SAW devices are also successfully developed by Achim Wixforth and collaborators for microfluidics acting both as pumps and as fluidic sensors aiming towards lab-on-a-chip applications. Based on these devices Advalytix started to market as their first product microfluidic mixers for predominantly microbiological applications in 2003.

*Conducting nanostructures in accessible host systems*

The encapsulation of functional guests in nanoporous channel hosts such as zeolites or periodic mesoporous materials offers numerous opportunities for the generation of hybrid functional materials. Channel structures with controlled morphology such as oriented films can be formed using concepts such as self-assembly, non-covalent interactions, host-guest chemistry, and structural templates.

For many applications it is desirable to expand the scale of the oriented channel systems into the nanometer range. The group of Thomas Bein has recently examined the influence of processing conditions, including electric fields, on the morphology, structure and orientation of nanoporous micelle-templated silica films with accessible pore structures. Synchrotron diffraction data show the profound effects of electric fields on the evolution and orientation of the channel structure.

The encapsulation of conductive nanostructures in ordered mes-

oporous hosts was also studied in the group; for this purpose new synthetic methods for the selective confinement of the guest structures in the porous hosts were developed. Carbon filaments and nanotubes, metal nanowires and nanoarrays, and semiconducting nanoparticles and wires have been prepared in the mesoporous systems by selective functionalization of the host matrix, followed by restricted growth in the nanosized porous system.

*Synthesis of porous materials*

Thomas Bein's group also studies the nucleation and crystallization mechanisms of nanoscale porous crystals as well as the role of molecular templates for the growth of novel zeolite structures. In the field of zeolite synthesis, we have developed automated, parallel methodologies (e.g., with 48 parallel reactors) that allow us to access a range of synthetic parameters vastly greater than the range possible with manual techniques, for the synthesis of known and new materials, including aluminosilicates, aluminophosphates, and titanosilicates.

This methodology was recently applied to the investigation of inorganic-organic hybrid materials based on phosphonic and phosphonocarboxylic acids in combination with metal ions. Special attention was given to the use of amino bis(methylphosphonic) acids since they have been rarely investigated in the synthesis of metal phosphonates. A wide variety of layered and three-dimensional framework structures eveolve from these building blocks.

*Host-guest catalyst systems*

In mesoporous host systems, it is often desirable to control the interactions with the guests via modification of the molecular interface. In the group of Thomas Bein, a direct alkylation route for the silica walls of ordered mesoporous hosts with organic alkylating agents has been developed. It can be shown that the direct formation of Si-carbon bonds is possible under appropriate conditions, resulting in a wide variety of surface-modified periodic channel structures with high organic linker density. With these tools at hand, building blocks for the construction of more complex and hierarchical nanoscale structures are now becoming accessible. This approach is exemplified with the attachment of amino acid residues that act as catalysts for crossed enantioselective aldol reactions.

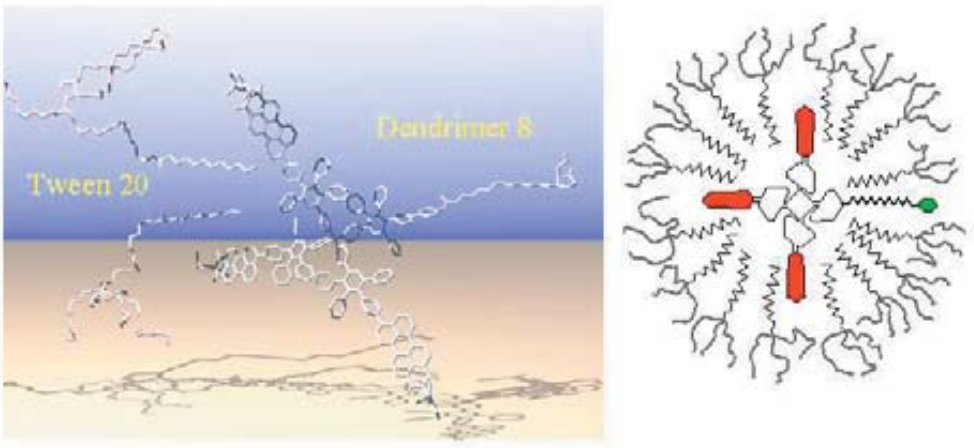
*Coating of semiconductor and metal hydrophobic nanocrystals with an amphiphilic polymer shell as a general route to water soluble nanocrystals*

Colloidal inorganic nanocrystals are promising materials because of their unique size-dependent properties. Highly crystalline and monodisperse nanocrystals are often synthesized at high temperature and their surface is coated with surfactants that render them hydrophobic. In a cooperation project of Wolfgang Parak, Andrey Rogach and Joachim Rädler a general route for converting hydrophobic nanocrystals into hydrophilic particles, which is a prerequisite

for their biological applications, is developed. High quality $CoPt_3$, Au, CdSe/ZnS, and $Fe_2O_3$ nanocrystals have been water-solubilized by wrapping a layer of amphiphilic polymer around the particles. The amphiphilic molecules intercalate the original hydrophobic surfactant layer with their hydrophobic portion ant ensure water solubility of nanocrystals with their hydrophilic groups. Analysis with transmission electron microscopy, gel electrophoresis, and fluorescence correlation spectroscopy demonstrates that narrow size distribution of the particles is conserved upon phase transfer to aqueous solution.

*Tetraarylmethanes with chromo- and electrophore sidechains - syntheses and intramolecular electronic communication of tetrahedral arranged π-systems.*
The group of Thomas J.J. Müller focuses here on the synthetic access to threedimensional nanometer-sized conjugated molecules with tetrahedral symmetry. The ensemble electronic properties reveal a significant electronic coupling between the four electrophor branches. A perspective of these novel molecules is the use in OLED or OFET as tetrafunctional emitter, electron or hole transport layers. Plans for self-assembly and nanostructuration of these 2-4 nm sized molecular entities are currently under way.

*Phenothiazinyldiades and -triades and Polymeric Phenothiazines as models for coupled Redox-addressable molecular wires*
These projects, also carried out in the group of Thomas J.J. Müller, encompass the synthetic access to oligophenothiazines with nanometer-sized dimension. Electronically, these redox active oligomers display a strong electronic coupling as shown by cyclic voltammetry in the ensemble. First measurements of the current-voltage behavior in a hole-only OLED have displayed excellent hole conductor properties. Thiolated oligo(phenothiazines) can be successfully self-assembled on gold plates and electrodes. Synthetically, we now have an access to all kind of functionalized electronically modified derivatives. Even organic-organometallic hybrid systems that now allow to fine-tune important molecular electronic properties such as oxidation potential, absorption or emission, are readily available. Characterization of materials properties of oligophenothiazines are still under investigation.
The experience of this project is applied to the synthesis of phenothiazine polymers and their structural, electronic and self-assembly characterization. Currently, Thomas J.J. Müllers group is able to synthesize structurally well-defined monodisperse oligomers up to a length of 6 nm. The ultimate goal is the incorporation of these organic wires into break junctions or between nanotweezers.
Furthermore, the group of Thomas J.J. Müller has synthesized (Oligo)phenothiazine-$C_{60}$-diades. (Oligo)phenothiazines are excellent fine-tunable donors. Therefore (Oligo)phenothiazine-$C_{60}$-arrays were synthesized to study Photoinduced Electron Transfer(PET) and, ultimately, to develop swichtable photoconductors and photovoltaic model systems.



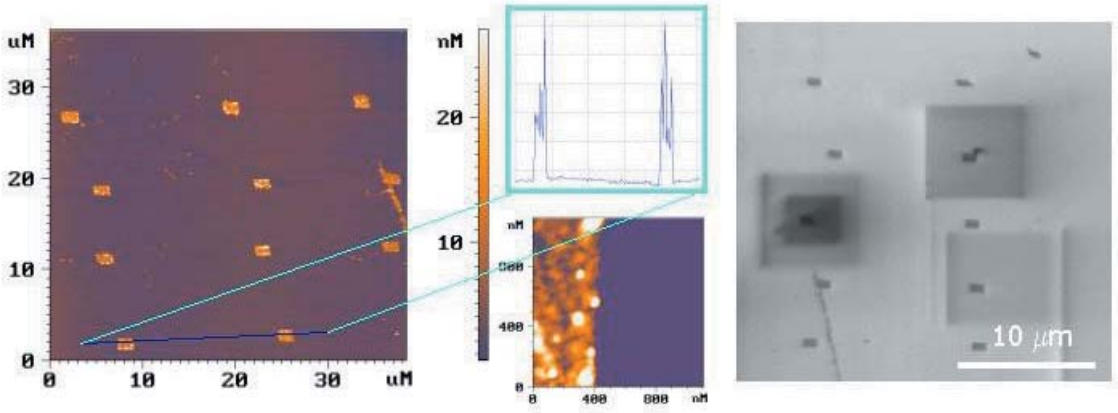

Surfactant stabilized dendrimers act as shape persistent nanoparticles with a well defined number of ligands (J. Rädler)

*Assembly of dendrimers*

Dendrimers are synthetic nanostructures with well defined size, chemical composition and steric architecture. In collaboration with the MPI-Mainz (AG Müllen), Joachim Rädler's group investigated the assembly of dendrimers with functional chemical groups with detergent. The dendrimer consisted of a polyphenylen core that carried three chromophores and a biotin linker. The existence of surfactant stabilized dendrimers with monodispoerse size distribution and enhanced biochemical reactivity were found.

*Nanolithography and Nanochemistry*

Nanolithography and the controlled build-up of small but controlled structures are important techniques in nanotechnology. There is at present an enormous drive in science towards the development of routes for the miniaturization of devices with novel applications, e.g. high-density data storage and biological detector arrays. In the group of Ulrich Schubert, Scanning Probe Techniques are utilized for the fabrication of nanometer-sized structures on octadecyl trichlorosilane (OTS) passivated silicon wafers. By applying a bias voltage on a conductive AFM-tip, the OTS layer on the surface can be oxidized locally. The oxidation changes the local properties of the surface, thus opening routes to controlled surface modification via both absorption as well as chemical modification routes. Recently the group of Ulrich Schubert has explored the possibility to greatly enhance the possibility for chemical modification by using a converting the oxidized patterns to acid anhydrides facilitating room temperature coupling of, for example, amines. This method has been used in first attempt to locally pattern surfaces with fluorescent dyes. Work is combined with the use of automated scanning probe nanolithography in an attempt to locally modify substrates with macroscopic dimensions.




A 10 × 10 array of 1.5 × 1 µm2 areas has been prepared by automated scanning probe nanolithography. The oxidized template has been covered by cationic gold nanoparticles (U. Schubert).

*Self-organization of Metallo-supramolecular Block-Coploymer Architectures*

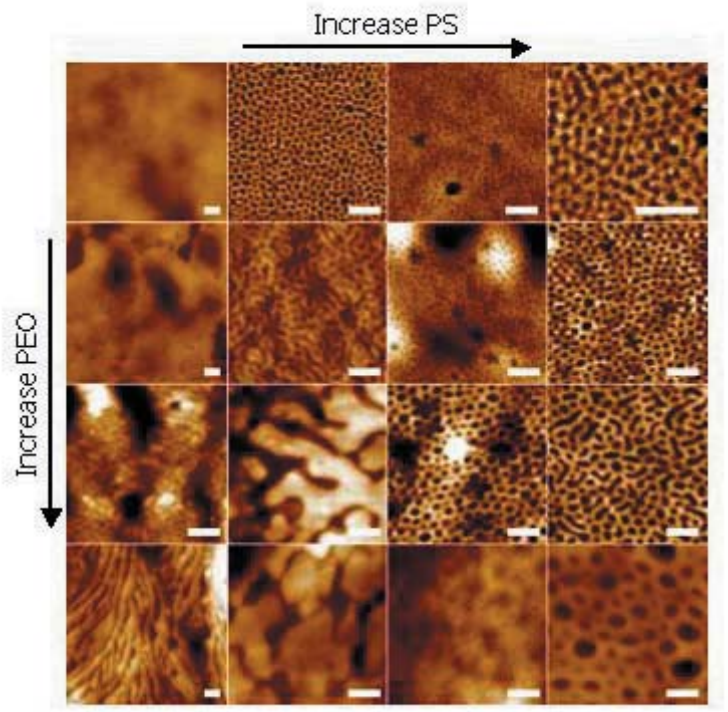
The specific affinity of bipyridine and terpyridine ligands for transition metal complexes was utilized as new "smart" connection point between molecules, polymers and nano-objects. Besides functionalized fullerene units, conducting moieties or protein recognition groups also the self-organization of nano-particles was studied. The method was used in order to assemble macromolecules: Suitable functionalized polymers (decorated with terpyridine units) were combined to A-A, A-B, AB-C (graft) block copolymers and other architectures. The synthesis and combination of four suitable "A"-blocks and four "B"-blocks resulted in a 4×4 library of AB-block copolymers with varying molecular weight and block ratios. Scanning probe microscopy studies on thin spin-casted films of polyethylene glycol-block-polystyrene were performed in the group of Ulrich Schubert, giving insight into the phase separation behavior of these materials.

*Assembly of carbon nanotubes and nanoscale molecular assemblies*

In the group of Udo Beierlein and Jörg Kotthaus, electronic transport properties of organic material, such as individual carbon nanotubes (CNTs) and nanoscale ensembles of phenylene-based conjugated molecules are studied. One of the major issues of using carbon nanotubes in electronics is the difficulty to align and contact single nanotubes. Therefore, both CNTs and gold electrodes on a silicon substrate were functionalized chemically. This resulted in an enhanced affinity of the negatively charged CNTs to the positively charged electrodes.

In order to measure the electronic transport properties of nanoscale ensembles of self-assembled mono- and multilayers of thiol- and isocyanide-terminated molecules, gold electrodes with contact distances of a few nanometers were fabricated by using a thin $Al_2O_3$ layer as a spacer between the electrodes. The thin oxide layer and the monolayers of molecules were characterized in collaboration with Bert Nickel

using X-ray reflectivity measurements. Some of the molecules studied were synthesized in Ulrich Schubert's group at Eindhoven. At low temperatures and as function of applied voltage the measured electronic conductances of such molecular ensembles exhibit characteristic structures the origin of which is also theoretically explored by Robert Dahlke and Ullrich Schollwöck.




Library of A-B block coploymers imaged by AFM (bar is 100 nm). On the horizontal axis the polystyrene block-weight is increased, vertically the polyethylene oxide is increased (U. Schubert).

*Studies of Single Molecules with STM-techniques*

Bianca Hermann studies large molecules with scanning tunneling microscopy (STM) over a wide temperature range in her group. Utilizing molecular self-organization on a graphite surface conformational analysis of single molecules in near atomic resolution was performed at room temperature and in air. The molecules, synthesized in Edwin Constable's group, Basel, are a flexible, aromatic-rich system of functionalized Fréchet-type dendrimers ideally suited to visualization by tunneling methods. In solution such a molecule has in principle many possibilities of arranging its functional groups, hence, many molecular conformations could occur. As a consequence of restricting the molecules to 2-D. by forming a self-organized monolayer on a surface one would expect only one conformation to be present which belongs to the global energy minimum. However, a range of conformations is found in co-existing surface-bound domains. Even with time none of the domains each comprising only a single molecular conformation wins over the other. An advanced modelling of the observed electronic states of the molecules is part of a collaboration with Robert Dahlke und Ulrich Schollwöck.

*Studies of protein-unfolding with AFM: combined imaging and unfolding*

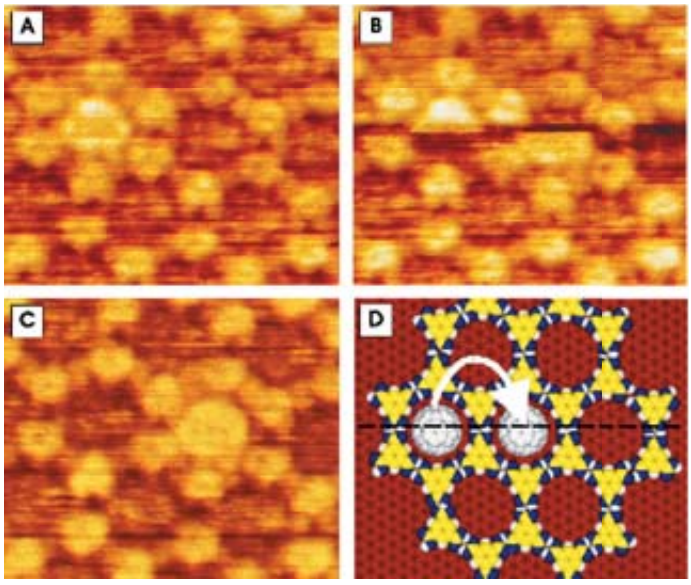
The combination of high-resolution atomic force microscopy (AFM) imaging and single-molecule force- spectroscopy was employed by Max Kessler and Hermann Gaub in collaboration with Daniel Müller (MPI Dresden) and Dieter Oesterhelt (MPI Martinsried) to unfold single bacteriorhodopsins (BR) from native purple membrane patches at various physiologically relevant temperatures.

The unfolding spectra reveal detailed insight into the stability of individual structural elements of BR against mechanical unfolding. Intermittent states in the unfolding process are associated with the stepwise unfolding of α-helices, whereas other states are associated with the unfolding of polypeptide loops connecting the α -helices.

It was found that the unfolding forces of the secondary structures considerably decreased upon increasing the temperature from 8 to 52°C. Associated with this effect, the probability of individual unfolding pathways of BR was significantly influenced by the temperature.

*STM imaging and manipulation of single molecules*

STM imaging and manipulation of single molecules such as Buckminsterfullerenes C60, coronen dye molecules and others as well as nanoclusters (eg. Au) have been performed at the solid liquid interface by the group of Wolfgang Heckl. In collaboration with partners (e.g. group of Prof. Feldmann concerning fluorescent nanoparticles) different guest molecules have been periodically ordered in arrays with nanometer lattice constants, using our organic molecular host template method. Together with Advalytics a method for incorporation of minute amounts of molecules in guest structures is being devised.




Playing Nanosoccer: STM topograph of the starting situation with a single C60 guest molecule inside the TMA host network ((a) – (c): 4.6 x 4.6 nm²); (b) manipulation step: after half the molecule was scanned the tunneling current was switched from imaging (IT≈70pA) to manipulation (IT≈150pA) conditions; after the molecule was transferred to the adjacent cavity the imaging conditions were restored (c) final result of the lateral manipulation with the whole molecule imaged in the target cavity (d) illustration of the TMA network and the manipulation process; the horizontal line indicates the lines which were scanned with an increased reference current

*Manipulation of nanostructures*

The tribology and nanomanipulation group of Robert Stark focuses on the investigation of different methods for the manipulation of smallest objects and structures. Research is carried out in close collaboration with the group of Wolfgang Heckl. The main research goal of the group is to understand friction and wear as it occurs for example during a nanomechanical manipulation. New developed nanoanalytical methods based on control engineering methods ensure enhanced speed and higher accuracy for measurements of material properties such as viscoelasticity on the nanometer scale. Dynamic atomic-force microscopy methods are investigated from a system theoretic point of view in collaboration with the groups of Reinhard Guckenberger in Martinsried and Ferdinand Jamitzky. The main focus of the Nano-bioinformatics group of Ferdinand Jamitzky is the theoretical analysis, simulation and prediction of nanostructures. For that purpose methods from the theory of dynamical systems, statistical data analysis techniques and molecular simulations are applied to problems in nano-science.

The main research goal of the group is to obtain a better theoretical understanding of processes between molecular and macroscopic length scales. Research projects include investigations of dynamical properties of the AFM from a system theoretic point of view (collaboration with

Robert Stark), simulation of the dynamics of mono-molecular layers (with Stefan Griessl and Frank Trixler) and development of classification methods for AFM-images of nano-fossils (with Andre Kempe).

*Single Virus Tracing*

Viruses play a major role in biology and medicine. A detailed analysis of the different steps of a viral infection is not only necessary to understand viral biology, but also for the development of efficient antiviral drugs and save viral gene therapy vectors. Single Virus Tracing by the group of Christoph Bräuchle allows visualization of the infection pathway of an individual virus labelled with fluorescent dye molecules (even in the case of labelling with a single dye molecule). The fluorescence of the marker molecule is imaged and used to follow the pathway of the virus with high spatial (40 nm) and time (10 ms) resolution (Science, 294 (2001)1929). As a first model system the infection pathway of Adeno-associated viruses (AAV) into HeLa cells has been investigated. AAV shows promising results for the use in gene therapy applications. A sequence of events can be tracked starting with a virus approaching the cell surface, successive receptor binding, membrane penetration, endosome formation and trafficing, virus release from the endosome and virus trafficking in the cytoplasm as well as penetration into the nuclear area.
Besides AAV the studies have been extended to other viral particles like HIV. HIV is an enveloped virus, which was labeled at its matrix protein (MA) and its viral protein (Vpr) with GFP and GFP mutants. After analyzing trajectories of single HI-Viruses, we can give a detailed kinetic picture of the membrane interactions leading to fusion. Comparing the behaviour of HIV on cells in absence and presence of anti HIV drugs the fusion inhibition of the pharmacon can be reproduced.

*Optical sectioning by structured illumination (OSSI)*

Optical sectioning by structured illumination is a wide-field microscopy technique with high axial resolution and a high frame rate compared to scanning confocal microscopy. With these capabilities the OSSI technique, applied in the groups of Christoph Bräuchle and Andreas Zumbusch, is the perfect completion of the Single Virus Tracing (SVT) technique, because it delivers a further improved image of the target cell structures the virions interact with. The changes on the SVT setup are minor. A grid in the illumination pathway is projected into the focal plane to "label" the information emerging from there with a striped pattern. A slight translation of the grid between the acquisition of two images only changes the intensity distribution in the focal plane, unwanted out-of-focus blur remains the same in both frames. Therefore calculating the difference between these two images removes the blur, only the information from the focus results in a signal. For a complete thin section, three images must be acquired with slightly translated grid to remove the patterned illumination.
This technique is used in fluorescence mode with stably transfected cell lines expressing fluorescent proteins which highlight microtubules,

actin filaments or the nucleosol. The viruses cannot be followed with this technique because they diffuse too quickly through the thin focal plane and would be visible only in one or two frames. In a typical experiment first a three dimensional image of the target cell structures is recorded (OSSI), then the grid is removed from the illumination path and the virus trajectories are recorded in SVT mode.

*Total-Internal-Reflection Fluorescent Microscope*
A sensitive microscope capable of measuring the dynamics of single molecules is currently being constructed by Don Lamb's and Christoph Bräuchle's groups. The system will be capable of performing single-molecule measurements both in vitro and in living cells.

*Coherent Anti-Stokes Raman Scattering (CARS) Microscopy*
During the last decade, different techniques of non-linear optical microscopy have become versatile tools for cell microscopy. The latest addition to this list is Coherent Anti-Stokes Raman Scattering (CARS) microsopy. Compared to other non-linear mircroscopies, CARS microscopy has the big advantage of offering chemical sensitivity, i.e. the presence of vibrational bands is monitored directly and no external labeling is necessary. Therefore, microscopical investigations can be performed under the most benign experimental conditions.
Three-dimensional CARS microscopy has first been demonstrated with a pulsed fs-laser system. In CARS microscopy, the reduction of the non-resonant background signal is of utmost importance. In the group of Andreas Zumbusch a new, simple, and straightforward approach, to achieve this goal has been developed. With that approach, the bandwidth of broad-band fs-laser pulses is spectrally focussed onto the vibrational resonance under investigation. For this purpose, the excitation pulses are chirped in order to keep their instantaneous frequency difference constant. Spectral features that are 100 times narrower than the excitation bandwidth are easily resolved. With this new development, the application of CARS microscopy to the ultrasensitive mapping of small, physiologically important molecules in live cells and tissues is within reach.

*Single molecule spectroscopy at cryogenic temperatures with vibronic excitation*
Low temperature single molecule spectroscopy experiments often rely on excitation from the purely electronic zero-phonon-line (ZPL) and collecting the Stokes shifted fluorescence. However, a major problem of this technique is that only exceptionally photostable systems can be studied. Because the absorbing zero-phonon-line is so narrow, already small spectral jumps (>30 GHz) in absorption lead to a loss of the excitation. For this reason the groups of Christoph Bräuchle and Andreas Zumbusch has developed vibronic excitation combined with spectrally resolved zero-phonon-line detection as a novel technique for single molecule spectroscopy at cryogenic temperatures. In contrast to ZPL excitation, vibronic excitation benefits from large absorption bands (broadened by 1-10 ps lifetimes and phonon sidebands) allow-

ing for investigation of large spectral jumps. First experiments with this setup were performed on terrylenediimide (TDI) molecules highly diluted in hexadecane (Shpol'skii matrix) or PMMA (polymer) matrices. As expected for an amorphous host, we found that under comparable excitation conditions TDI molecules exhibited more frequent spectral jumps in PMMA than in hexadecane. In this host, large spectral jumps on the order of 80 cm-1 were recorded together with small spectral changes. This technique promises applications in spectroscopy of a wide-range of molecular systems including fluorescing proteins.

*FCS and Pulsed Interleaved Excitation*

Fluorescence correlation spectroscopy (FCS) and fluorescence resonance energy transfer (FRET) are methods currently used by the groups of Christoph Bräuchle and Don Lamb to probe the dynamics of biomolecules and nanomachines. Time-correlated single-photon counting (TCSPC) measures the arrival time of a detected photon to better than 50 ps resolution. When pulsed laser sources are used, TCSPC provides information over the lifetime of the fluorophore. When two or more pulsed lasers are interleaved, the arrival time of the fluorophore also indicates which laser excited the molecule. The additional information allows removal of spectral cross-talk from two color detection in FCS cross-correlation experiments. In single molecule FRET measurements, the molecule brightness of both donor and acceptor can be determined, leading to more accurate determination of the FRET efficiency. Additionally, molecules that contain both a donor and acceptor but show minimal energy transfer can be distinguished from molecules missing an acceptor.
In the Rädler group fluorescence correlation spectroscopy was applied to study the dynamics of large linear macromolecules in solution. The technique proofed valuable to access the intramolecular dynamics of actin and lambda-phage DNA.

*Basics of tapping mode AFM*

Part of the AFM work of Reinhard Guckenberger is devoted to a better understanding of the tapping mode. For tapping in air, it was found that measurements of the whole frequency spectrum of the cantilever motion allows one to analyze the tip sample interaction in detail and to understand the imaging behaviour of the tapping AFM. This work is supported by a collaboration with the group of W. Heckl, especially with R. Stark, concerning model calculations and interpretation of the results.

*Scanning near-field optical microscopy (SNOM) in fluorescence*

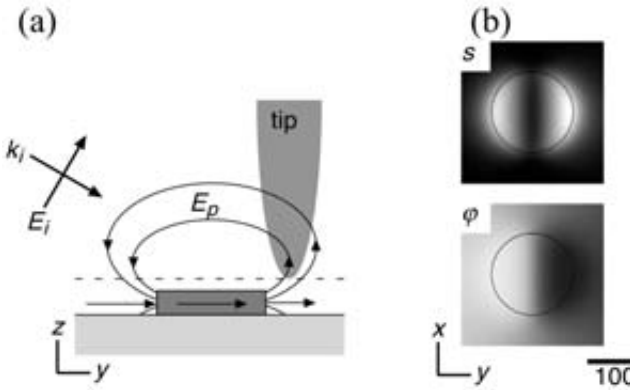
Fluorescence allows easy identification of labelled spots of biological specimens. Compared to the confocal laser scanning microscope, SNOM achieves a higher resolution and allows to acquire a topographical signal simultaneously with the optical signal which facilitates interpretation of the images. To minimize bleaching of fluorophores, the aperture SNOM is best choice, but the scattering SNOM achieves higher resolution. Reinhard Guckenberger's group combined the advantages

of the both types of SNOM by producing a metal tip on the aperture of a conventional fiber tip. With this new kind of probe they achieved in fluorescence a resolution of about 20 nm and were able to image single fluorophores. The first step of the production of the extra metal tip is to grow an electron beam deposited (EBD) tip which was done in collaboration with the group of Bert Lorenz. The EBD tip consists mainly of carbon and is finally coated with metal.

*Near-field optical and infrared microscopy*

Apertureless scattering-type optical near-field microscopy allows to measure and map the local optical property of a sample, with a spatial resolution limited by the width of the probing tip, about 20 nm. The group of Fritz Keilmann has shown that a carbon nanotube tip can well serve this purpose. The interesting outlook is that even much finer, molecularily defined carbon nanotube tips can be expected to provide ideally sharp, robust sensors for both topographical and optical sample properties.

We further showed that scattering-type optical near-field microscopy can indeed operate even with long-wavelength ($\lambda \approx 10$ µm) infrared illumination with no deterioration in spatial resolution, and with no different contrast mechanism. Of course, the existence of vibrational resonances makes the infrared very attractive for the ongoing development of a chemical nanoscope, where by choice of a vibrationally resonant illumination one can highlight any specific chemical compound in the image.




Dipolar optical field pattern of a plasmon-resonant Au disk (λ =633 nm). (a) Schematic side view of incident plane wave $E_i$, of the particle's eigenfield $E_p$, and of the probing tip. (b) Top view of near-field amplitude (upper row) and phase (lower row) of the fields' z-component, from exact electrodynamic calculation. (c) Experimental amplitude $E_2$ and phase $\Phi_2$ images using a carbon nanotube tip as near-field scattering optical probe (F. Keilmann)

nanotype was founded in 2000. It had a staff of 15 full time employees and developed multiplexed protein biochip assays for drug development and diagnostics, based on its highly sensitive molecular force test technology. nanotype secured several patents amd was able to publish its new technology in high ranking scientific journals. Unfortunately, nanotype had to shut down operations in September because it could not close its 2nd round of financing.

In 2003 Advalytix and Nanion succesfully introduced their first products into the market and attocube, ibidi, and nanotools continue to grow by selling their respective products.

# Selected Publications of 2003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„Architecture of the RNA polymerase II-TFIIS complex and implications for mRNA cleavage“
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„Low temperature single molecule spectroscopy using vibronic excitation and dispersed fluorescence detection“
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# Theses finished in 2003

*Doctoral Theses*

Christoph Bödefeld
Opto-Akustisches Pumpen von Halbleiter-Quantenpunkten

Stefan Griessl
Two-dimensional Architectures of Organic Adorbates, A STM, TDS, LEED and Force Field Calculation Study

André Kempe
Nanostructures in Precambrian Fossils

Christa S. Krämer
Di- und Triphenothiazine – Neue Modellsysteme für redoxschaltbare molekulare Drähte

Hans-Jörg Kutschera
Lineare und nichtlineare akustophotoelektrische Wechselwirkung – Oberflächenwellen und photogenerierte Ladungsträger in Halbleiterquantenstrukturen

Markus Lackinger
Investigations of organic adsorbates on crystalline substrates with STM

David Müller
Herstellung photovernetzbarer, heterostrukturierter organischer Halbleiterbauteile aus Lösung

Laura Pescini
Electromechanical coupling and dissipation mechanisms in nanoscale systems

Christian Schäflein
Elektronische Eigenschaften und Manipulation von Carbon Nanotubes

Eva Weig (neé Höhberger)
Phasen- und Dissipationseffekte in 3D-nanostrukturierten Systemen

*Diploma Theses*

Peter Bantzhaff
Entwicklung einer Methode zum Nachweis von Wasser in extraterrestrischen Bodenproben durch Untersuchungen fluviatiler und glazialer Feldspat- und Quarzsandkörner mittels Licht-, Rasterelektronen- und Rasterkraftmikroskopie

Sebastian Bauer
Synthesis and characterization of inorganic-organic hybrid materials based on $H(HO_3PCH_2)_2N(H)CH_2C_6H_4COOH$ using high-throughput methods

Guido H. Clever
Neuartige Tetra(hetero)arylmethane als redoxaktive Nanomoleküle

Stefan Frei
Investigations of Dendritic Sediments, A new method for the proof of existance of water on mars

Harald Graser
STM of RNA-bases as a precambrian model system

Paul Hix
Development and experimental use of a STM for extraterrestrial applications in microgravity

Constanze Höhberger
Nano-opto-mechanische Systeme

Johann Jaud
Optische und mechanische Charakterisierung einzelner molekularer Motoren

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Thermal Desorption Spectroscopy of Trimesic Acid on Au(111)

Robert Kraus
LEED investigations of Trimesic Acid on Gold(111) and Graphite (0001)

Martin Kuba
Synthesis and analysis of CTAC templated mesoporous thin films and the effect of an electric field during synthesis

Ferdinand Kühner
Affinitätsmessungen zwischen Aptameren und Proteinen mit Hilfe eines Kraftmikroskops

Tobias Lindenberg
Akustoelektrische Sensoren für fluidische Anwendungen

Karin Memminger
Synthese von o- und m-phenylenverbrückten Oligophenothiazinen - Versuche zur Synthese cyclischer Oligophenothiazine

Stefanie Mugrauer
Fluoreszenzmikroskopische Untersuchungen einzelner HIV-Partikel unter besonderer Berücksichtigung der Virus-Zellmembran-Wechselwirkung

Clara Sattler
Einzelmoleküluntersuchungen von superhelikalen Proteinfilamenten

Alexandra Scherer
Single Molecule Force Spectroscopy on Polysaccharides

Daniel Schröer
Elektronische Transporteigenschaften freitragender Phononenkavitäten

Stefan Seidl
Photonenstatistik an selbstorganisierten Quantendots

Ken Yasuda
Microporous catalytic combustion sensors – Devices and novel composite materials

Peter Zehetmayer
Das Monomer des Lichtsammelkomplexes Phycoerythrocyanin: Optische Experimente am Ensemble, an einzelnen Molekülen und Modellierung des Energietransferverhaltens

# Submitted Patents

H. Gaub, F. Oesterhelt, C. Albrecht, B. Steipe, M. Cieplik, H. Clausen-Schaumann
*Verfahren zum Nachweis von Mutationen bei einer Nukleinsäure*
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*Verfahren zur Markierung von Gegenständen*
DE 10205506

# Awards

Prof. Patrick Cramer
EMBO long-term fellowship (A. Meinhart) 2003
Boehringer Ingelheim PhD fellowship (T. Kamenski) 2003

Dr. Niels Fertig
IKuh-Award (Nanotechnology-Award), 1st prize

Dr. Rainer Hillenbrand
IKuh-Award (Nanotechnology-Award), 3rd prize

Prof. Matthias Rief
Nanowissenschaftspreis 2003

Prof. Ulrich Schubert
NWO VICI award

Dr. Robert Stark
BMBF Young Scientist Competition „Nanotechnology"
http://www.fz-juelich.de/wing/index.php?index=29

Prof. Achim Wixforth
First BioTrends Award 2003
http://www.biotrends.de/biotrends/html/award.htm

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DAAD - Deutscher Akademischer Austausch Dienst http://www.daad.de/

DFG-Sonderforschungsbereiche SFB 413, SFB 455, SFB 486, SFB 563, SFB 631 http://www.dfg.de

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Dutch Polymer Institute (DPI) http://www.polymers.nl/PRO1/general/default.htm

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# Joint Projects for Education and Training

Osaka University - EU - LMU Forum 2003 on Nanoscience and Nanotechnology

CeNS Winterschool "Current Issues of Nano-Bio-Science"

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"CeNS meets Industry"

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