

PAN-EUROPEAN RESEARCH IN CHEMISTRY

CERC3 has established a co-operative framework among the CERC3 research council chemistry committees which aims to support trans-national research projects in universities. The vision is to provide some national chemistry committee support for individual national research groups to become engaged in trans-European projects, thereby bringing together a mix of different skills and research facilities necessary to address the research aims.

The chemistry committees will also co-operate in the assessment of research proposals, which would be carried out by peer review, ideally using a mutually agreed selection of international referees. CERC3 has drawn up a set of key principles which govern the assessment framework. To help get the initiative started a series of workshops have been held to consider and identify research opportunities in particular areas of emerging chemistry. It is expected that these workshops will lead to the promotion of trans-European research teams to focus on specific research problems and for these to be the subject of research proposals for consideration by the appropriate CERC3 research councils. A pilot initiative was launched in Autumn 1999.

THE FUTURE

Promotion of European chemistry for:

- ★ Competitiveness in research
- ★ Greater public awareness and understanding the benefits of research and development in chemistry
- ★ Alignment with chemistry's importance for health and medical care, for the creation of new materials to improve quality of life and safety of industrial manufacture.

For further information on CERC3 please visit the CERC3 website at www.cerc3.net or contact the secretary
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CERC 3

Chairmen of the European
Research Councils' Chemistry Committees



Nanoscience

"From chemistry and molecular microscopy
to design of functional surfaces"



CHALMERS

CERC-3

Chairmen of the European Research Councils' Chemistry Committees

Workshop

Nanoscience:

“From chemistry and molecular microscopy to design of functional surfaces”

Göteborg Sweden
April 11th - 13th 2003

Organized by the Department of Physical Chemistry
Chalmers University of Technology
412 96 Göteborg - Sweden

The Workshop is supported
by the Nobel Institute of Chemistry Stockholm, Sweden

Local CERC3 Adviser

Professor Bengt Nordén
in partnership with Annie Dalbera - in charge of the European affairs.

Workshop Organizer

Professor Owe Orwar
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PROGRAM

THURSDAY APRIL^{10th}

Location: Reception Hall, Palmstedtsalen, Main Entrance Chalmers University of Technology

16.00-18.00 Welcome Reception and Registration

FRIDAY APRIL^{11th}

Location: Palmstedtsalen, Main Entrance Chalmers University of Technology

- 8.20 Welcome Address by Professor Jan-Eric Sundgren, *President, Chalmers University of Technology, Sweden*
- 8.25 Introductory Remarks by Professor Owe Orwar, *Chalmers University of Technology, Sweden*
- 8.30 **PLENARY LECTURE**
Richard N. Zare, *Stanford University, USA*
Trapping Single Cells for Analysis Using Microfluidic Devices Fabricated with Multilayer Soft Lithography
- 9.15 Bo Albinsson, *Chalmers University of Technology, Sweden*
Mediated Electronic Coupling: Controlled Energy and Electron Transfer in Porphyrin-Based Donor-Bridge-Acceptor Systems
- 9.35 Davide Barreca, *Università di Padova, Italy*
Metal Oxide Nanosystems by CVD and Sol-Gel Bottom-Up Approaches
- 9.55 Sarah L. Heath, *University of Manchester, UK*
Shedding Light on Biological Systems: The Development of Dinuclear Lanthanide Probes
- 10.15 **Break, Refreshments & Coffee**
- 10.35 Muriel Blanzat, *Université Paul Sabatier, France*
Cationic Amphiphiles Analogues of HIV Cellular Receptor Galactosylceramide
- 10.55 Donna A. Chen, *University of South Carolina, USA*
Studies of the Growth and Reactivity of Oxide-Supported Metal Nanoparticles as Models for Heterogeneous Catalysts
- 11.15 Albert Schenning, *Eindhoven University of Technology, The Netherlands*
Towards Supramolecular Electronics
- 11.35 Christian G. Claessens, *Universidad Autónoma de Madrid, Spain*
Sub-Phthalocyanines: Nonplanar Aromatic Compounds as Building Blocks in Supramolecular Chemistry

- 11.55 Rainer Jordan, *Technische Universität München, Germany*
Structuring of Polymer Brushes on the Nanometer Scale
- 12.15 **Lunch**
- 13.15 **PLENARY LECTURE**
Josef Michl, *University of Colorado, USA*
Artificial Surface-Mounted Molecular Rotors
- 14.00 Juan Casado Córdón, *Universidad de Málaga, Spain*
Quinoid Oligothiophenes: from Amphoteric Molecules to Transistor Devices
- 14.20 Todd Emrick, *University of Massachusetts, USA*
Novel Functional Polymers and Nanoparticles with Interfacial Activity
- 14.40 Roland Gamsjäger, *University of Linz, Austria*
Oriented Binding of the Carboxyl-Tail of the L-type Ca^{2+} Channel for AFM- and SPR-Experiments
- 15.00 Lev D. Gelb, *Washington University, St. Louis, USA*
Multiscale Modeling of Xerogels and Aerogels
- 15.20 **Break, Refreshments & Coffee**
- 15.40 Zoran Konkoli, *Chalmers University of Technology, Sweden*
Simplified Model of the Cell: Molecular Transport and Reactions in Restricted Geometries
- 16.00 Rainer Haag, *Albert-Ludwigs Universität, Germany*
Dendritic Polymer Architectures for DNA- and Drug-Delivery
- 16.20 Johan Bergenholtz, *Göteborg University, Sweden*
Depletion Interactions in Colloidal Systems
- 16.40 Stefan Hecht, *Freie Universität Berlin, Germany*
Design and Manipulation of Molecular Nano-objects
- 17.00 **Break, Beverages & Fruit**
- 17.20 Fredrik Höök, *Chalmers University of Technology, Sweden*
Lipid-Based Sensor Templates
- 17.40 Mogens Brøndsted Nielsen, *University of Southern Denmark, Denmark*
Acetylenic Scaffolds of Tetrathiafulvalene
- 18.00 Mats Lundberg, *Lund University of Technology, Sweden*
Synthesis and Catalysis of Crystalline Mesoporous High Surface-Area Cerium Dioxide

END OF DAY ONE

SATURDAY APRIL^{12th}

Location: Palmstedtsalen, Main Entrance Chalmers University of Technology

- 8.30 **PLENARY LECTURE**
Kazuhiko Kinoshita, *Okazaki National Research Institutes, Japan*
Chemo-Mechanical Coupling in F₁-ATPase, a Rotary Motor Made of a Single Protein Molecule
- 9.15 Myrtil Kahn, *Laboratoire de Chimie de Coordination, Toulouse, France*
Synthesis and Physical Properties of Metal Oxide Nanoparticles
- 9.35 Christine D. Keating, *The Pennsylvania State University, USA*
Exploiting Aqueous Phase Separation for Functional Microscale Architectures
- 9.55 Holger Schönherr, *University of Twente, The Netherlands*
AFM and Soft Materials Approaches in Nanoscience: From Chemical Reactions on the Nanometer Scale to Probing Individual Host-Guest Complex Rupture Events
- 10.15 **Break, Refreshments & Coffee**
- 10.35 Harm-Anton Klok, *Max Planck Institute For Polymer research, Mainz, Germany*
Hybrid Block Copolymers Containing Protein Folding Motifs
- 10.55 Mikael Käll, *Chalmers University of Technology, Sweden*
Optical Properties and Applications of Gold and Silver Nanoparticles
- 11.15 Philippe Leclère, *University of Mons-Hainaut, Mons, Belgium*
Semiconducting Nanostructures Obtained by Self-Assembling Processes
- 11.35 José R. Galán-Mascarós, *Universidad de Valencia, Spain*
Dual-Function Molecular Materials: Design of Conducting Ferromagnets
- 11.55 A.E. Rowan, *University of Nijmegen, The Netherlands*
Catalytic Rotaxanes; Mimicking Nature's Processive Catalysts
- 12.15 **Lunch**
- 13.15 **PLENARY LECTURE**
Fraser Stoddart, *Department of Chemistry, UCLA, USA*
Meccano on the NanoScale: A Blueprint for Making Some of the World's Tiniest Machines
- 14.00 Björn Åkerman, *Chalmers University of Technology, Sweden*
Electrophoretic Migration of DNA in Lyotropic Liquid Crystals
- 14.20 Stefan Mecking, *Albert-Ludwigs-Universität, Germany*
Hybrids of Metal Nanoparticles with Highly Branched Amphiphilic Macromolecules. Synthesis, Properties and Potential Applications
- 14.40 Francesco Mercuri, *Università di Perugia, Italy*
MD Simulations of a [2]Catenane-Based Molecular Switch

- 15.00 Pierre Mobian, *Université Louis Pasteur, Strasbourg-Cedex, France*
Synthesis and Photochemical Properties of a [2]-Catenane Constructed around a Ru(Diimine)₃²⁺ Complex Used as a Template
- 15.20 **Break, Refreshments & Coffee**
- 15.40 Gábor Molnár, *Laboratoire de Chimie de Coordination, Toulouse, France*
Spin-Crossover Complexes: Towards Molecular Electronic Devices
- 16.00 Maija Nissinen, *University of Jyväskylä, Finland*
Alkyl Resorcinarenes and Pyrogallarenes as Structural Subunits for Self-Organising Molecular Assemblies
- 16.20 Francesca Nunzi, *Università di Perugia, Italy*
The Coordination Chemistry of Carbon Nanotubes: a Density Functional Study through a Cluster Model Approach
- 16.40 J.L. Toca-Herrera, *Universität für Bodenkultur, Wien, Austria*
Hollow Polymeric Capsules Covered with S-layers
- 17.00 **Break, Beverages & Fruit**
- 17.20 J.H.R. Tucker, *University of Exeter, UK*
Photochromic and Chromogenic Supramolecular Switches
- 17.40 M. Wilhelm, *Max-Planck-Institut für Polymerforschung, Mainz, Germany*
Reorientation in Block Copolymer Melts as Detected on-line via FT-Rheology and External 2D-SAXS
- 18.00 Thomas Ederth, *Linköping University, Sweden*
Forces In and Between Self-Assembled Monolayer Structures
- 19.45 **Workshop Dinner Arranged by Göteborg City Council**

END OF DAY TWO

SUNDAY APRIL^{13th}

Location: Palmstedtsalen, Main Entrance Chalmers University of Technology

- 8.30 **PLENARY LECTURE**
Jean-Marie Lehn, *Université Louis Pasteur, Strasbourg, France*
Nanoscience and Nanotechnology by Self-Organization
- 9.15 Owe Orwar, *Chalmers University of Technology, Sweden*
Life-Like Nanotechnology: Soft-Matter Nanofluidic Devices by Self-Assembly & Self-Organization.
- 9.35 Henrik Ottosson, *Uppsala University, Sweden*
Novel σ -conjugated Wires: A Quantum Chemical Study of their Stabilities and Charge Transport Abilities
- 9.55 Bernadette Quinn, *Helsinki University of Technology, Finland*
Monolayer Protected Clusters as Tunable Multi-Valent Redox Species
- 10.15 **Break, Refreshments & Coffee**
- 10.35 Anders E.C. Palmqvist, *Chalmers University of Technology, Sweden*
Nanostructured Materials by Surfactant Self-Assembly and Solvothermal Synthesis
- 10.55 Christophe Petit, *Université Pierre et Marie Curie, Paris, France*
Collective Magnetic Properties in Organization of Cobalt Nanocrystals
- 11.15 Jon Preece, *University of Birmingham, UK*
Toward Nanostructuring SAMS by X-Ray Irradiation Inducing Specific Chemical Transformations: The First Example of the Chemical Modification of an Organic Nitro Thin Film to an Organic Amine Thin Film by X-ray Photoelectron Irradiation on a SiO₂ Surface
- 11.35 Joachim P. Spatz, *University of Heidelberg, Germany*
Molecularly Defined Rigid c(RGDfK) Nano-Templates Regulate Cell Adhesion by Control of $\alpha\upsilon\beta$ 3-Integrin Clustering
- 11.55 **Lunch**
- 12.40 **PLENARY LECTURE**
George M. Whitesides, *Harvard University, Cambridge, USA*
Unconventional Nanofabrication
- 13.25 J.C. Rodrigues, *University of Madeira, Funchal, Portugal*
Synthesis and Characterization of Metallodendrimers With Potential Nonlinear Optical Applications
- 13.45 Christoph A. Schalley, *University of Bonn, Germany*
Supramolecular Chemistry Goes Gas Phase
- 14.05 Daniel T. Chiu, *University of Washington, Seattle, USA*
Micro- and Nano-Scale Chemical Analysis of Individual Subcellular Compartments

14.25 **Break, Refreshments & Coffee**

14.40 Panel Discussion with Plenary Speakers. Professor Bengt Nordén Moderator,
Chalmers University of Technology, Sweden

END OF WORKSHOP

Abstracts

Trapping Single Cells for Analysis Using Microfluidic Devices Fabricated with Multilayer Soft Lithography

Richard N. Zare
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We have developed a microfluidic device constructed from polydimethylsiloxane (PDMS) using multilayer soft lithography (MSL) for the analysis of single cells. The device contains integrated valves and pumps that enable rapid, accurate isolation of an individual cell from bulk solution and precise delivery of minute volumes of reagents to the selected cell. Various applications are demonstrated, including cell viability assays, ionophore-mediated intracellular Ca^{2+} flux measurements, and multi-step receptor-mediated Ca^{2+} measurements. These assays, and others, are achieved with significant improvements in reagent consumption, analysis time, and temporal resolution over macroscale alternatives.

A unique advantage of MSL fabrication is the ability to produce rapidly new device prototypes. By this means we have developed several related devices for different methodologies, including simultaneous perfusion of multiple cells with different reagents and “cell dispensing” to collection chambers for culture and harvest. Thus, the design described in this work is representative of a diverse family of devices that could be optimized for many different assays. Furthermore, each chip design could be scaled to accommodate hundreds of independent cell capture areas for use in high throughput applications. This combination of adaptability and scalability could potentially revolutionize the way cellular assays are performed.

This work has been carried out in collaboration with Fluidigm Corporation, South San Francisco, CA, whose support of these efforts is gratefully acknowledged.

MEDIATED ELECTRONIC COUPLING: CONTROLLED ENERGY AND ELECTRON TRANSFER IN PORPHYRIN BASED DONOR-BRIDGE-ACCEPTOR SYSTEMS

Bo Albinsson

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Understanding the mechanism for electronic coupling through molecules is important for modeling the electron and energy transfer processes in biological and biomimetic systems and also for the future construction of molecular scale electrical and logical networks. We have designed a set of tri-chromophoric donor-bridge-acceptor (D-B-A) molecules in which the mediation of singlet excitation energy transfer, triplet excitation energy transfer, and electron transfer are systematically studied as a function of the electronic structure of the bridging chromophore. Measurements of photoinduced excitation energy and electron transfer were performed by a combination of time-resolved and steady-state spectroscopic techniques, including picosecond transient absorption and emission. The transfer processes were further investigated by quantum chemical methods and the theoretical and experimental results are in harmony.

References:

- (1) Kilså, K.; Kajanus, J.; Macpherson, A. N.; Mårtensson, J.; Albinsson, B. *Bridge-Dependent Electron Transfer in Porphyrin-Based Donor-Bridge-Acceptor Systems* J. Am. Chem. Soc. **123** (2001) 3069-3080.
- (2) Andréasson, J.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *Triplet Energy Transfer in Porphyrin Dimers: Comparison Between π - and σ -Chromophore Bridged Systems*. J. Am. Chem. Soc. **122** (2000) 9844-9845.
- (3) Kyrychenko, A.; Albinsson, B. *Conformer-Dependent Electronic Coupling for Long-Range Triplet Energy Transfer in Donor-Bridge-Acceptor Porphyrin Dimers*. Chem. Phys. Lett. **366** (2002) 291.

Metal oxide nanosystems by CVD and sol-gel *bottom-up* approaches

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Nanosized materials (thin films, clusters, composites) based on metal oxides or sulphides have gained a markedly increasing consideration with regard to both scientific and applicative purposes. A current challenge in this field is to devise proper synthetic strategies providing tools for tailoring the material properties and functionality. Advanced trends in the synthesis of inorganic nanosystems are focused on *bottom-up* approaches in which suitable molecular precursors are used as building blocks in chemical pathways from molecules to organized systems. In this framework, Chemical Vapor Deposition (CVD) and sol-gel processes enable the design and chemical modification of composition, nanostructure and morphology of the final product by a suitable choice of the synthesis conditions and of the starting precursors. In particular, the synergy between plasma-assisted CVD processes and *soft* sol-gel syntheses may disclose interesting perspectives for a versatile modulation of the system characteristics.

This contribution is devoted to outlining some of our recent results in these fields, focusing particular attention on the nanosystem properties and their mutual relationships with the processing conditions. To this regard, a key-step is represented by an extensive chemical and physical characterization of the synthesized materials. Selected relevant results will be presented and discussed.

Shedding Light on Biological Systems: The Development of Dinuclear Lanthanide Probes

Dr Sarah L. Heath, Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL; email: sarah.l.heath@man.ac.uk

Luminescent lanthanide probes are convenient tools to investigate a variety of analytical and structural problems. For example, the need for new, non-radioactive, luminescent tags to develop sensitive fluorimmunoassays has prompted the search for new lanthanide complexing agents. Dinuclear lanthanide complexes are especially interesting as they not only supply two probe metals in one complex but also provide a way to study the intramolecular metal-to-metal charge transfer. To this end we have prepared a series of polydentate ligands based upon a phenol containing head group and coordinating pendant arms and have synthesised a number of novel dimetallic lanthanide complexes. Variation of the ligand pendant arms results in the formation of three structurally different complex types. The complexes display long luminescent lifetimes and have high quantum yields.

Catanionic Amphiphiles Analogues Of HIV Cellular Receptor Galactosylceramide

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Amphiphiles analogues of galactosylceramide play a key role in the inhibition of HIV-cell recognition. They interact with the viral glycoprotein gp120, permitting host-guest adhesion. To simplify the synthetic access of these compounds, we used the concept of catanionic surfactants to prepare easily accessible analogues of galactosylceramide(1). To optimise these antivirals it appeared essential to establish a correlation between the structure of the analogue, its aggregation behaviour and its antiviral efficiency.

Monovalent, divalent (geminis) and multivalent (dendrimers(2)) inhibitors have been synthesized to evaluate the importance of the multiplicity of active sites to limit the HIV infection. Enhancing the local density of active sites improved the biological activity but other parameters, like the lipophilicity of the analogue, had also an influence on it.

Modulation of the hydrophobicity of these analogues have been made to confirm this hypothesis. In fact, increasing the lipophilicity improved the antiviral activity, with a parallel increase of the cytotoxicity, which is related to the incorporation of the alkyl chains of the compound into the cell membrane. Nevertheless, for gemini analogues, alkyl chains are packed together to minimize their contact with water. The hydrophobic part is then masked, decreasing the ability of the chains to penetrate the cell membrane(3).

References:

- (1) Blanzat, M., Perez, E., Rico-Lattes, I., Promé, D., Promé, J.-C., Lattes, A. New catanionic glycolipids 1. Synthesis, characterization, and biological activity of double-chain and gemini catanionic analogues of galactosylceramide (gal β ₁cer). *Langmuir* **15**, 6163-6169 (1999).
- (2) Blanzat, M., Turrin, C.-O., Perez, E., Rico-Lattes, I., Caminade, A.-M., Majoral, J.-P. Phosphorus-containing dendrimers bearing galactosylceramide analogs: Self-assembly properties. *Chem. Commun.* **17**, 1864-1865 (2002).
- (3) Blanzat, M., Perez, E., Rico-Lattes, Lattes, A., Gulik, A. Correlation between structure, aggregation behaviour and cellular toxicity of anti-HIV catanionic analogues of galactosylceramide. *Chem. Commun.* **2**, 244-245 (2003).

Studies of the Growth and Reactivity of Oxide-Supported Metal Nanoparticles as Models for Heterogeneous Catalysts

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Metal particles supported on oxide surfaces serve as excellent model systems for developing a better understanding of commercial heterogeneous catalysts. We have investigated the growth of Cu and Ni nanoparticles on a TiO₂(110) surface by scanning tunneling microscopy (STM) under ultrahigh vacuum conditions ($P < 1 \times 10^{-10}$ Torr). In order to study potential particle size-dependent surface chemistry, we have developed a protocol for depositing metal particles with uniform size distributions. Narrow size distributions can be achieved when the rate of diffusion on the surface is slow compared to the deposition flux rate. Temperature programmed desorption studies of methanol reaction on oxidized Cu nanoparticles showed that methanol oxidation was not sensitive to the size of the particles; formaldehyde and water were the major desorption products observed for particles 30Å-80Å in diameter. However, STM experiments indicate that there is a major change in the morphology of the Cu particles during oxidation. The formation of Cu-O bonds appears to weaken the Cu-Cu bond, allowing two-dimensional Cu clusters to form on the surface at the expense of the existing three-dimensional clusters. This effect has also been observed for Ni particles, but the rate of particle dissociation is slower even though Ni is more easily oxidized than Cu.

Towards Supramolecular Electronics

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A unique construction process for supramolecular assemblies in the 10 - 100 nm length scale that are connected to electrodes and act as (opto)electronic components is aimed. At the moment there is no methodology to connect supramolecular structures to electrodes. However, this will be crucial for the success of supramolecular chemistry in the field of nanotechnology and nanosized electrooptical devices. This unexplored field of research is proposed to be called supramolecular electronics.¹

For the fabrication of these supramolecular electronic devices, π -conjugated oligomers have been synthesized, which self-assemble in a controlled fashion into (helical) wires.² In these stacks fundamental issues like light harvesting, exciton diffusion length and energy transfer processes within the nanometer dimensions are investigated. Additionally, electron transfer and the conversion of light into a chemical reaction or electricity is explored.³ These structures can be transformed to a solid support. This opens the way to sandwich these stacks between electrodes and study their electronic properties.

References:

- (1) Meijer, E.W., Schenning, A.P.H.J. Materials marriage in electronics, *Nature*, **419**, 353-354 (2002).
- (2) Schenning, A.P.H.J., Jonkheijm, P., Peeters, E., Meijer, E.W. Hierarchical Order in Supramolecular Assemblies of Hydrogen-Bonded Oligo(*p*-phenylene vinylene)s, *J. Am. Chem. Soc.*, **123**, 409-416 (2001).
- (3) Schenning, A.P.H.J., van Herrikhuijzen, J., Jonkheijm, P., Chen, Z., Würthner F., Meijer, E.W. Photoinduced electron transfer in hydrogen-bonded oligo(*p*-phenylene vinylene)-perylene bisimide chiral assemblies, *J. Am. Chem. Soc.*, **124**, 10252-10253, (2002).

Subphthalocyanines: Nonplanar Aromatic Compounds as Building Blocks in Supramolecular Chemistry

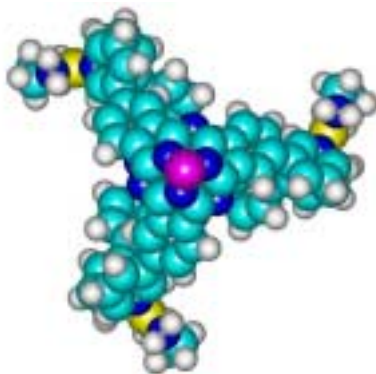
Christian G. Claessens

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Subphthalocyanines (SubPcs), lower homologues of phthalocyanines, are nonplanar aromatic macrocycles comprising three diiminoisoindole units *N*-fused around a boron atom. The 14 π -electron system characteristic of these compounds confers interesting optical properties that have been exploited in the fields of dyes, nonlinear optics and photonic devices.¹ Herein, we will present two aspects of the chemistry of SubPcs.

1. Aromaticity – Extended π -Surfaces. We synthesized a series of fused subphthalocyanine dimers, showing that this kind of binuclear system is actually formed as a mixture of two topoisomers that have been separated and characterized.² These fused homodimers were shown to display physical characteristics very different from the ones of their related SubPc analogues. These compounds are the first step towards the synthesis of larger curved π surfaces.

2. Metallo-supramolecular Chemistry. The intrinsic chirality of subphthalocyanines with C_3 or C_1 symmetries represents also a promising feature that enhances their potential as building blocks for the construction of complex molecules. A tris(3-pyridyl)-substituted C_3 symmetric subphthalocyanine was dimerized into a M_3L_2 cage in the presence of a stoichiometric amount of (en)Pd(NO₃)₂.³ NMR studies demonstrated the recognition event to be accompanied by chiral self-discrimination between the two enantiomers of the SubPc. Moreover, the specificity is such that only one of four possible isomers was detected in solution.



Top view of a [M₃L₂] homodimeric subphthalocyanine cage showing the C₃ symmetry of the supramolecular assembly

References:

- (1) Claessens, C. G., González-Rodríguez, D. & Torres T. Subphthalocyanines: singular nonplanar aromatic compounds – síntesis, reactivity, and physical properties. *Chem. Rev.* **102**, 835-853 (2002).
- (2) Claessens, C. G. & Torres T. Synthesis, separation and characterization of the topoisomers of fused bicyclic subphthalocyanine dimers. *Angew. Chem. Int. Ed.* **41**, 2561-2565 (2002).
- (3) Claessens, C. G. & Torres T. Chiral self-discrimination in a M₃L₂ subphthalocyanine cage. *J. Am. Chem. Soc.* **124**, 14522-14523 (2002).

Structuring of Polymer Brushes on the Nanometer Scale

Rainer Jordan

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For the preparation of functional nanostructures two principal approaches are available: First, the so called *bottom-up* approach, in which small molecules are either chemically linked or otherwise interconnected (self-assembled) to form a larger and possibly functional entity. In the second, the *top-down* approach one can cut-down a larger bulk material to a nanoscopic structure by e.g. engineering tools such as lithography.

The talk gives two examples to use self-assembly as the *bottom-up* **and** lithography as the *top-down* approach to prepare structured polymer brush layers on the microscopic and nanoscopic length scale:

a) Structured polymer brushes by surface-initiated polymerization (1): The synthetic concept of preparing dense polymer brushes on planar surfaces is described, in which self-assembled monolayers (SAM) of terminal functionalized thiols are used to initiate living anionic, cationic and (controlled) radical polymerization on planar substrates and nanoparticles. The very recent results on polymer brush systems structured on the micrometer as well as nanometer scale will be included in which we use *chemical lithography* to determine the locus of the surface-polymerization.

b) Lipopolymers (2): Lipopolymers are hydrophilic polymers bearing a hydrophobic head group such as a lipid or lipid analog. By the combination of specific lipid moieties and suitable polymers (poly(2-oxazoline)s), the properties of low molar mass lipids and macromolecules can be combined. The driving force for structuring is phase segregation and self-assembly of the amphiphilic molecule in a selective solvent. The impact of the hydrophilic hydrophobic balance of the lipopolymer and the sterical needs of the two moieties upon the layer morphology, dynamic and static swelling behavior as well as the highly dynamic wetting properties will be presented.

Recently, we used lipopolymers as tailored tethers for the construction of stable biomimetic cell membranes. The synthesis, preparation of structurally defined lipopolymer surfaces and the construction of biologically inspired surface coatings will be presented.

References:

- (1) U. Schmelmer, R. Jordan, W. Geyer, A. Götzhäuser, W. Eck, M. Grunze, A. Ulman, Patterned Polymer Brushes via Surface-initiated Photopolymerization on Self-assembled Monolayers Structured by Chemical Lithography, *Angew. Chem. Int. Ed.* **2003**, 42, 559-563.
- (2) a) R. Jordan, K. Martin, H. J. Räder, K. K. Unger, Lipopolymers for Surface Functionalizations: 1. Synthesis and Characterization of Terminal Functionalized Poly(N-propionylethylenimine)s, *Macromolecules* **2001**, 34, 8858-8865. b) A. Förtig, R. Jordan, O. Purruicker, M. Tanaka, 2-Alkyl-2-oxazoline Lipopolymers for the Construction of Polymer Tethered Lipid Bilayers, *Polymer Preprints* **2003**, in press. c) O. Purruicker, A. Förtig, R. Jordan, M. Tanaka, submitted.

Artificial Surface-Mounted Molecular Rotors

Josef Michl

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We are studying devices up to 1-3 nm in size, consisting of (i) an axle covalently attached either to a solid surface or to nodes in a grid with molecular-size openings and (ii) a part that is rotatable around the axle, with a small (“free rotors”) or significant (“switches”) barrier. We have fabricated and characterized azimuthal rotors (axle perpendicular to the surface; “landed helicopter”), and altitudinal rotors (axle parallel to the surface; “waterwheel”). We have performed molecular dynamics simulations of their individual motion in response to rotation-inducing (i) fluid flow or (ii) electric field. Phase diagrams describe rotor behavior as a function of field strength and frequency and elucidate the interplay of a driving force, molecular friction, thermal random motion, and intrinsic barriers. We are now attempting to fabricate regular two-dimensional grids, using the concept of a molecular “Tinkertoy” construction set, in order to mount dipolar rotors in hexagonal or rectangular arrays and examine their collective motions. Possible future applications will be outlined.

Quinoid Oligothiophenes: from Amphoteric Molecules to Transistor Devices

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An important goal for organic electronics is the synthesis of organic semiconductors with improved performance in thin film transistors [1]. This design process should consider both molecular properties and solid state packing to achieve materials with enhanced transport properties. We have found that certain quinoid oligothiophenes might be oxidized and reduced [2,3]. Thus one might devise ambipolar organic devices (p- and n-type semiconductors) by using them.

These quinoid oligothiophenes display reversible electrochemical reduction and oxidation in solution and form π -stacks in the solid state. The ease of reduction and the π -stacking guided us to develop a thin film transistor that turned out to work as a n-conductor (with an electron mobilities of 0.005 cm²/Vs, one order of magnitude higher than those previously reported). Here, we study the molecular keys that make this material behaves as n- or p-channel conductor using electrochemical, spectroscopic (UV-Vis-NIR, IR and Raman), and spectroelectrochemical techniques in combination with quantum chemistry. We conclude that the precise understanding of the molecular properties and structure leads to the realization of macroscopic properties that indeed give rise to the construction of a broader variety of circuit architectures for electronic applications.

References:

- (1) Katz, H. E., Bao, Z. & Gilat, S. L. Synthetic chemistry for ultrapure, processable, and high-mobility organic transistor semiconductors. *Acc. Chem. Res.* **34**, 359-369 (2001).
- (2) Pappenfus, T. M., Chesterfield, R. J., Frisbie, C. D., Mann, K. R., Casado, J., Raff, J. D. & Miller, L. L. A π -stacking terthiophene-based quinodimethane is an n-channel conductor in a thin film transistor. *J. Am. Chem. Soc.* **124**, 4184-4186 (2002).
- (3) Casado, J., Miller, L.L., Mann, K.R., Pappenfus, T.M., Higuchi, H., Ortí, E., Milián, B., Pou-Amérigo, R., Hernández, V. & López Navarrete, J.T. Quinonoid oligothiophenes as electron-donor and electron-acceptor materials. A spectroelectrochemical and theoretical study. *J. Am. Chem. Soc.* **124**, 12380-12388 (2002).

Novel Functional Polymers and Nanoparticles with Interfacial Activity

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Materials that exhibit interfacial activity can be used for a variety of purposes, for example in separations and as surfactants, in self-assembly processes to provide ordered nanostructures, and in the construction of new materials that utilize the self-assembly of chemically functionalized materials. This presentation will highlight recent work in the synthesis of amphiphilic polymers and nanoparticles, with an emphasis on their activity at the interface of immiscible fluids.¹⁻³ In particular, polyolefins that are made hydrophilic through particular types of pendant substitution show an excellent affinity for the oil-water interface. In addition, luminescent cadmium selenide nanoparticles, when properly functionalized, show a preference for the oil-water interface to give self-assembled nanostructures. The character of these nanostructures is controlled by the types and sizes of the polymers and/or nanoparticles used, the ligand environment on the nanoparticles, and the choice of oil phase used in the assembly process.

References:

- (1) Yao Lin, Habib Skaff, Todd Emrick, Anthony D. Dinsmore, and Thomas P. Russell, Nanoparticles at Liquid-Liquid Interfaces: Assembly, Displacement and Transport *Science* **299**, 226-229 (2003).
- (2) Habib Skaff and Todd Emrick, A Rapid Route to Amphiphilic Cadmium Selenide Nanoparticles Functionalized with Poly(ethylene glycol) *Chem. Comm.* 52-53 (2003).
- (3) Habib Skaff, M. Firat Ilker, E. Bryan Coughlin, and Todd Emrick, The Preparation of Cadmium Selenide-Polyolefin Composites from Functional Phosphine Oxides and Ruthenium-based Metathesis *J. Am. Chem. Soc.* **124**, 5729-5733 (2002).

Oriented binding of the carboxyl-tail of the L-type Ca^{2+} channel for AFM- and SPR-experiments

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Ca^{2+} -induced inactivation of L-type Ca^{2+} channels protects the cell from being overloaded by Ca^{2+} . This mechanism is mediated by the Ca^{2+} -dependent interaction of motifs of the carboxyl-tail of the channel with calmodulin (CaM). In order to obtain a more detailed picture of this interaction using AFM and SPR, a surface anchoring protocol for oriented functionally proteins derived from the carboxyl-tail (containing all necessary binding motifs to CaM) on a gold surface was developed. The proteins containing His₆-tags were bound onto NTA-thiols, which were covalently attached to ultraflat flame-annealed gold surfaces. Thiols containing triethylene-glycol-groups instead of NTA-groups were used as matrix-thiols in the SAM (self assembled monolayer) to minimize unspecific binding. This protein array was characterized by AFM and the functionality of the protein regarding the binding ability to CaM was verified by SPR using Biacore SIA kit gold chips which were functionalized with NTA- and matrix-thiols. In addition, SPR-measurements with the carboxyl-tail immobilized onto a lipid-monolayer consisting of POPC and NTA-lipids on a Biacore HPA chip were carried out to compare thiol-anchoring with anchoring via lipids. Force-spectroscopy experiments in the presence of Ca^{2+} using the more stable thiol-protein-array and CaM bound via a flexible crosslinker onto a functionalized cantilever were performed.

Multiscale modeling of xerogels and aerogels

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A multiscale approach is taken in computational studies of the structure and properties of sol-gel derived materials and nanocomposites. These techniques can be used to investigate both silica xerogels and aerogels and materials composed of titania and other oxides; they can also be extended to materials with metallic or metal-oxide nanoparticle inclusions and to carbon nanotube/aerogel nanocomposites. Such materials may find application in catalysis, optics, and electronics, and also have desirable properties when prepared as thin films.

For the treatment of the atomic-scale structure of such materials, realistic molecular simulations can be used. However, gel-derived materials also have important structure features on scales up to tens of nanometers, and gel aging and drying processes involve large-scale, slow physics for which coarse-grained methods must be employed.

We have developed a particulate model which consists of “gel particles” which interact via short-ranged potentials and move under the influence of a solvent background. The solvent is modeled as a lattice-gas that exhibits the liquid-vapor equilibria and surface tension forces necessary to describe gel collapse during drying.

Simplified model of the cell: molecular transport and reactions in the restricted geometries

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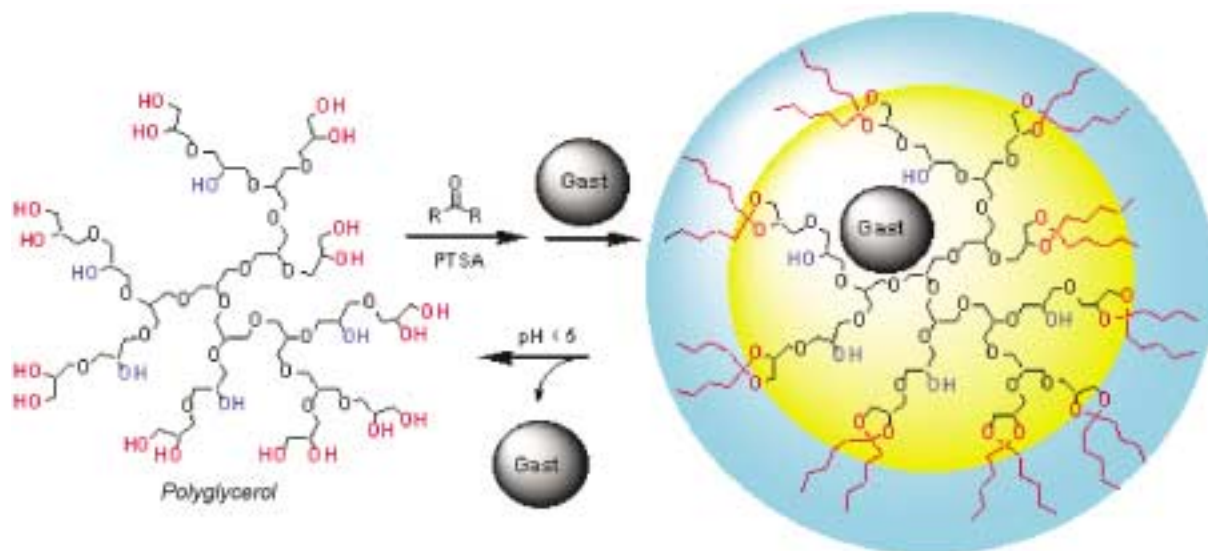
Cell is a factory of chemical reactions: reactants enter, participate in reactions, and products are moved somewhere else, exactly at the place where they are needed. Clearly, in order to grasp workings of the cell there are many issues that need to be understood. In the talk I will focus on three: (i) transport of the reactants, (ii) reactions in very small volumes (restricted geometries), and (iii) synchronization of (i) and (ii). I will mainly discuss (i) and (ii). In connection with (ii) I will first demonstrate an approximate solution of the A+B reaction-diffusion model. The A+B model is defined on the lattice where particles A and B (assumed to be point like objects) jump randomly in all directions (diffusion) and when within reaction range react with certain probability. I will show that average number of particles decays in time exponentially, using pair-like approach. If time allows I will comment on the recent theoretical work on the macromolecular translocation which deals with a particular form of (i); the polymer passing through a narrow hole which is embedded into the membrane.

Dendritic Polymer Architectures for DNA- and Drug-Delivery

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During the last decade the interdisciplinary interest in multifunctional dendritic macromolecules increased due to their potential applications, such as carrier for organic substrates, drugs and catalysts. In contrast to dendrimers, hyperbranched polymers, such as polyglycerol and polyethylenimine are readily available in large quantities.¹ By using these hyperbranched core-structures, it is now possible to create a dendrimer-like core-shell architecture which are based on the chemical differentiation between linear OH (NH)-functionalities and terminal 1,2-diols (NH₂-groups).² After selective protection of the terminal groups, it has been possible to modify the core with several functional groups to obtain selectively core-functionalized structures. By deprotection of the terminal groups, several dendritic architectures with a hydrophobic core and hydrophilic shell can be prepared. Also, encapsulation, transport and pH-triggered release of encapsulated polar guest molecules (DNA, dyes and drugs) has been achieved.³ A similar behavior is observed, when hyperbranched polyethylenimine is used as a core-structure. These dendritic polyamine architectures can also be employed for the transport of oligonucleotides and DNA for gene transfection.



References:

- (1) H. Frey, R. Haag, in *Encyclopedia of Materials, Science and Technology*, Elsevier, Oxford, 2001, 3997.
- (2) R. Haag, J.-F. Stumbé, A. Sunder, H. Frey, A. Hebel, *Macromolecules*, **2000**, *33*, 8157.
- (3) M. Krämer, J.-F. Stumbé, R. Haag, et al., *Angew. Chem. Int. Ed.* **2002**, *41*, 4252.

Depletion interactions in colloidal systems

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Addition of non-adsorbing polymer provides a means of tuning the interactions among colloidal particles in a relatively controlled manner. The underlying mechanism is a depletion of polymer for entropic reasons in regions between closely spaced particles, which causes an effective colloid-colloid attraction. In this talk I will summarize our work on depletion-induced colloidal attractions, which includes the modeling of polymer-containing microemulsions and the development of theory for polymer-containing hard-sphere dispersions. The former study¹ demonstrates that depletion can be called upon to explain quantitatively the gradient diffusion of microemulsion droplets, and in the latter collaborative study^{2,3} we elucidate the nature of the transitions to colloidal gels that result on addition of sufficient amount of polymer.

References:

- (1) Zackrisson, M., Andersson, R. & Bergenholtz, J. Depletion interaction in model microemulsions, *to be submitted*.
- (2) Pham, K. N. *et al.* Multiple glassy states in a simple model system. *Science* **296**, 104-106 (2002).
- (3) Bergenholtz, J., Poon, W. C. K. & Fuchs, M. Gelation in model colloid-polymer mixtures. *Langmuir*, *in press*.

Design and Manipulation of Molecular Nanoobjects

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The realization of devices based on the action of few or even single molecules represents an attractive target and yet a significant scientific challenge of the nanotechnological revolution.¹ Molecular building blocks with an inherent function that can be organized and specifically addressed are at the heart of this bottom-up approach.²

Here, initial efforts toward the chemical synthesis of functional organic nanotubes, their characterization and manipulation as well as investigation of structure-property relationships will be described. Polymerization of suitable functional monomers leads to a polymer strand (primary structure) that folds into an ordered helical conformation³ (secondary structure), and after covalent stabilization by intramolecular cross-linking as well as inner/outer post-modification affords an addressable nanotube of defined dimension and functionality. This concept is inspired by the structural evolution in Nature. Approaches to control the nanotubes' properties as well as attempts to visualize and rationally manipulate these and other nanosized objects will be discussed.

References:

- (1) Special Issue: Nanotechnology. *Sci. Am.* **285**, 32-91 (2001), and references therein.
- (2) Hecht, S. Welding, Organizing, and Planting Organic Molecules on Substrate Surfaces—Promising Approaches towards Nanoarchitectonics from the Bottom up. *Angew. Chem. Int. Ed.* **42**, 24-26 (2003), and references therein.
- (3) Hill, D. J., Mio, M. J., Prince, R. B., Hughes, T. S. & Moore, J. S. A Field Guide to Foldamers. *Chem. Rev.* **101**, 3893-4011, (2001), and references therein.

Lipid-based sensing templates investigated using combined quartz crystal microbalance and surface plasmon resonance measurements

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Supported lipid-assemblies, being either planar bilayers on e.g. SiO₂ or intact vesicles, are interesting candidate systems for controlled immobilization of a large range of biomolecules, including oligonucleotides, small peptide fragments and both water-soluble as well as transmembrane proteins. Specific focus in this presentation will be put on how quartz crystal microbalance data conducted simultaneously with surface plasmon resonance data under identical flow geometry improves the interpretation of planar lipid-bilayer formation and subsequent streptavidin binding, DNA coupling and DNA hybridization, including results on how proper control of the state of streptavidin arrangement improve measurements on bio-recognition kinetics.ⁱ Furthermore, these lipid- and protein-based immobilization strategies have been extended towards DNA-functionalized gold spots and/or nanometer-sized gold particles,ⁱⁱ in both cases surrounded by inert planar lipid bilayers. Examples will be presented on how these templates can be used for spatial-directed coupling of DNA-tagged lipid vesicles,ⁱⁱⁱ carrying either single-chain Fv antibody fragments (scFv) or the transmembrane proteins: proton-translocating nicotinamide-nucleotide transhydrogenase and the glycerol facilitator GlpF, which is a membrane-channel protein of the aquaporin family.

References:

- ⁱ⁾ Larsson, C. and Höök, F. *Characterization of DNA immobilization and subsequent hybridization on a 2D arrangement of streptavidin on a lipid bilayer supported on SiO₂*, submitted.
- ⁱⁱ⁾ Olofsson L., Rindzevicius T., Pfeiffer I., Käll M. and Höök F. *A Surface-Based Gold-Nanoparticle Sensor for Specific and Quantitative DNA Hybridization Detection*. submitted.
- ⁱⁱⁱ⁾ Svedhem S., Pfeiffer I., Larsson C., Wingren C., Borrebaeck C., Höök F. *Patterns of DNA-labeled and scFv-antibody carrying lipid vesicles directed by preferential protein and DNA adsorption/binding and supported lipid bilayer formation on an Au/SiO₂ template*. *ChemBioChem*; 2003, in press.

Acetylenic Scaffolds of Tetrathiafulvalene

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Tetrathiafulvalene (TTF) is a reversible, two-electron donor that has been intensively studied for almost three decades, mainly with the aim of developing low-temperature organic superconductors, but also as an important redox-active unit in supramolecular chemistry.¹ Combined with the three reversible redox states of TTF, the engineering of switchable nonlinear optical (NLO) materials is also of major focus. A lot of structural variation of the parent TTF system has been carried out, in particular by insertion of π -conjugated spacers between the two 1,3-dithiole units.

In this work, a selection of mono- and diacetylenic dithiafulvalenes was synthesized and employed for construction of linearly extended TTFs with hexa-2,4-diyne-1,6-diylidene or deca-2,4,6,8-tetrayne-1,10-diylidene spacers.² By stepwise acetylenic scaffolding³ of a (*E*)-1,2-diethynylethene (DEE) unit, an extended TTF containing a total of 18 sp/sp² carbons in the spacer was prepared. Synthetic protocols for obtaining TTF derivatives with a diethynyl-substituted alkene spacer were also developed. Electrochemical investigations show that structural changes in the spacer as well as lateral functionalization strongly influence the position of the first and second oxidation potentials of these large π -conjugated TTFs and the degree of reversibility.

References:

- (1) Nielsen, M. B. *et al.* Tetrathiafulvalenes as building blocks in supramolecular chemistry. *Chem. Soc. Rev.* **29**, 153-164 (2000).
- (2) Nielsen, M. B. *et al.* Novel Extended Tetrathiafulvalenes Based on Acetylenic Spacers: Synthesis and Electronic Properties. *Chem. Eur. J.* **8**, 3601-3613 (2002).
- (3) Nielsen, M. B. & Diederich, F. The Art of Acetylenic Scaffolding: Rings, Rods, and Switches. *The Chemical Record* **2**, 189-198 (2002).

Synthesis and Catalysis of Crystalline Mesoporous High Surface-Area Cerium Dioxide

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Mesoporous thin films of cerium dioxide were prepared by using a copolymer surfactant (Pluronic 123) at ambient conditions with alcohol as a solvent. The material was produced via a direct calcination step, without the necessity of a gelling stage. The synthesised CeO₂ matrix was crystalline with a high surface area and pores of nanometer dimensions. The material was characterised by scanning electron microscopy, transmission electron microscopy, powder X-ray diffraction, and determination of the specific surface area after the BET method.

Catalytic properties and thermal stability were studied in films with different BET specific surface area. The catalytic conversion of carbon monoxide to carbon dioxide and how thermal treatments of the catalysts influence the catalytic properties have been investigated. Light-off temperature measurements were performed using a plug flow micro reactor made in quartz glass only. When comparing the catalytic properties associated with a specific structure or morphology directly, it was found that the proportion of {100} surfaces determine the catalytic properties of the material and these surfaces become important at calcination temperatures between 773 K and 973 K.

Chemo-Mechanical Coupling in F_1 -ATPase, a Rotary Motor Made of a Single Protein Molecule

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The central γ subunit of F_1 -ATPase rotates against a surrounding cylinder made of $\alpha_3\beta_3$ subunits. This rotary motor is powered by sequential ATP hydrolysis in the three β subunits, and reverse rotation of the motor is expected to cause ATP synthesis. We have shown, by single-molecule imaging, that (i) the rotary torque is nearly independent of the rotation angle, (ii) 80-90 pN nm of mechanical work can be done per ATP hydrolyzed, (iii) binding of ATP causes $\sim 90^\circ$ rotation, and (iv) release of the last hydrolysis product causes further $\sim 30^\circ$ rotation. Points ii implies that the efficiency of chemo-mechanical conversion may reach $\sim 100\%$. Points i-iv allowed us to infer the angle-dependent potential energies for γ rotation for each of chemical intermediates that appear during rotation. I will show a model, based on these potential energies, that can explain how the free energy of ATP hydrolysis may be converted to mechanical torque, and more importantly, how the reverse rotation of the motor by an external force may lead to ATP synthesis. The most important aspect of our experimental finding, represented in the model, is that binding (and release) of a nucleotide, rather than hydrolysis *per se*, is the major source of mechanical output. An equally important corollary is that mechanical motion (rotation) changes the affinity for a nucleotide by orders of magnitude, the essential ingredient of Boyer's binding-change model for ATP synthesis. We have now shown, using magnetic tweezers, that reverse rotation of F_1 indeed produces ATP. Possibly for the first time, energetically uphill chemical synthesis has been accomplished by the action of mechanical force generated by human artefacts (with the aid of the nature's nano machine). If time allows, I will also show that we can now image binding and release of fluorescent ATP, distinguishing the three binding sites on a single F_1 molecule.

Synthesis and physical properties of metal oxide nanoparticles

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Since nanosciences have been recognized as an important area for future developments in technologies, chemists are engaged in researches for the design of nanoobjects leading to the desired nanomaterials. Among those materials, oxides present a large variety of interesting physical properties like magnetism, luminescence or semi-conduction. Those properties can be varied depending on the composition, the size and the shape of the particles.

We will illustrate our research concerning the design of metal-oxide nanoparticles and the monitoring of their physical properties focussing on few examples.

Exploiting Aqueous Phase Separation for Functional Microscale Architectures

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When two chemically dissimilar polymers are mixed in aqueous solution, phase separation can occur. We are interested in aqueous two-phase systems (ATPS) both as scaffolds for biorecognition-driven nanoparticle assembly and as a primitive functional model of the cytoplasm. (1) We have assembled metallic nanowires at the interface of a poly(ethyleneglycol)/dextran ATPS, and have demonstrated that nanowire-bound DNA retains its ability to selectively hybridize at this interface. Our goal is to realize *deterministic* assembly of functional, anisotropic building blocks by confining assembly to a two-dimensional interface and controlling the temporal sequence of assembly events through hybridization temperature/sequence. Striped nanowires offer several opportunities as building blocks; their length, width, and composition can be controlled as desired, for example to tailor electrical properties. Specific assembly targets include function blocks for integration into molecular electronic memory and logic devices. (2) We have synthesized giant unilamellar lipid vesicles containing an ATPS that exhibits temperature-dependent phase behavior. Vesicles are prepared above the phase transition temperature and cooled to initiate ATPS formation. These structures are exciting in that they enable for the first time the interior volume of liposomes to be structured, and biomolecules to be partitioned among the encapsulated microphases.

References:

- (1) Helfrich, M. R., Mangeney-Slavin, L. K., Long, M. S.; Djoko, K. Y. & Keating, C. D. Aqueous phase separation in giant vesicles. *J. Am. Chem. Soc.* **124**, 13374-13375 (2002).
- (2) Nicewarner-Peña, S. R. *et al.* Submicrometer metallic barcodes. *Science* **294**, 137-141 (2001).
- (3) Nicewarner-Peña, S. R., Raina, S., Goodrich, G. P., Fedoroff, N. V. & Keating, C.D. Hybridization and extension of Au nanoparticle-bound oligonucleotides. *J. Am. Chem. Soc.* **124**, 7314-7323 (2002).

AFM and Soft Materials Approaches in Nanoscience: From Chemical Reactions on the Nanometer Scale to Probing Individual Host-Guest Complex Rupture Events

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Atomic force microscopy (AFM) and self-assembly-based soft materials approaches can be exploited in nanoscience for surface patterning and templating on nanometer length scales (1). In these areas, AFM, as one of the workhorses of emerging nanotechnology, is widely applied both as nanolithographic tool and indispensable molecular scale characterization technique. In this presentation the focus is set on the application of chemically functionalized AFM probe tips in unraveling chemical reactivity at soft, i.e. organic or polymeric, surfaces at the nanometer scale. By following pull-off forces of AFM tips functionalized with reactive self-assembled monolayers (SAMs), reaction kinetics on the sub-100 molecule scale can be followed in real-time (2). The correlation of reactivity with molecular order, as assessed on average by FTIR spectroscopy, the determination of activation energies, as well as the elucidation of reaction mechanisms, will be discussed for SAMs of terminal esters on gold. Finally, the unbinding forces in host-guest complexes of various guests in surface-immobilized beta-cyclodextrin, as measured by AFM-based single molecule force spectroscopy, will be reported. A correlation of equilibrium complexation constants and single host-guest complex rupture forces is observed. The loading rate-independence of these systems is in contrast to most biological systems reported so far and can be attributed to quasi-thermodynamic conditions of the experiments.

References:

- (1) Schönherr, H., Paraschiv, V., Zapotoczny, S., Crego-Calama, M., Timmerman, P., Frank, C. W., Vancso, G. J., Reinhoudt, D. N. Unraveling the Nanostructure of Supramolecular Assemblies of Hydrogen-Bonded Rosettes on Graphite: An Atomic Force Microscopy Study *Proc. Natl. Acad. Sci. USA* **99**, 5024-5027 (2002).
- (2) Schönherr, H., Chechik, V., Stirling, C. J. M., Vancso, G. J. Monitoring Surface Reactions at an AFM Tip: An Approach To Follow Reaction Kinetics in Self-Assembled Monolayers on the Nanometer Scale *J. Am. Chem. Soc.* **122**, 3679-3687 (2000).
- (3) Schönherr, H., Beulen, M. W. J., van Veggel, F. C. J. M., Bügler, J., Huskens, J., Reinhoudt, D. N., Vancso, G. J. Individual Supramolecular Host-Guest Interactions Studied by Dynamic Single Molecule Force Spectroscopy *J. Am. Chem. Soc.* **122**, 4963-4967 (2000).

Hybrid block copolymers containing protein folding motifs

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Amphiphilic block copolymers are well-known for their ability to self-organise into vesicles or micelles or to form hydrogels.(1) Generally, the self-assembly of such block copolymers is driven by unspecific hydrophobic interactions. As a result, control over nanoscale supramolecular organisation is limited. In this contribution, a new class of polyethyleneglycol (PEG)-b-peptide block copolymers is presented. The peptide segments in these block copolymers are derived from protein folding motifs and can mediate self-assembly not only via unspecific hydrophobic interactions, but also via specific and/or directed hydrogen-bonding and coulombic interactions.(2) As an example, PEG-b-peptide copolymers based on the coiled-coil motif will be presented.(3) The block copolymers are prepared via solid phase synthesis. Circular dichroism and analytical ultracentrifugation experiments indicate that the self-assembly properties of the peptides are retained upon conjugation of the PEG block and that the block copolymers self-organise into discrete supramolecular aggregates. The results demonstrate that the ability of peptide sequences to self-assemble hierarchically into well-defined higher-order structures can be transferred onto hybrid block copolymers. Since most polymers are amorphous, or at most semi-crystalline, the combination of protein folding motifs with synthetic polymers may allow the development of hierarchically organised polymeric materials with unprecedented levels of structural control.

References:

- (1) Rösler, A., Vandermeulen, G.W.M., Klok, H.-A. Advanced drug delivery devices via self-assembly of amphiphilic block copolymers. *Adv. Drug. Deliver. Rev.* **53**, 95-108 (2001).
- (2) Klok, H.-A. Protein-inspired materials: synthetic concepts and potential applications. *Angew. Chem. Int. Ed.* **41**, 1509-1513 (2002).
- (3) Klok, H.-A., Vandermeulen, G.W.M., Rösler, A. Poly(ethylene glycol) block copolymers containing protein folding motifs. *Polym. Prepr.* **43(2)**, 715-716 (2002).

Optical properties and applications of gold and silver nanoparticles

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Gold and silver nanoparticles exhibit brilliant colors due to so-called Localized Surface Plasmon Resonances (LSPR). The resonance wavelengths are extremely sensitive to the size, composition and shape of the nanoparticle, as well as to the optical properties, e.g. refractive index, of the immediate surrounding. Moreover, excitation of a LSPR results in an enormous enhancement of the local optical intensity near the particle surface. It is now possible to control these properties by modern nanofabrication methods, such as electron beam or colloidal lithography (1). I will describe some recent results on LSPR effects from Applied Physics, Chalmers. Examples include applications in biosensing, nanooptics (2), and surface-enhanced spectroscopy (3).

References:

- (1) J. Aizpurua, P. Hanarp, D.S. Sutherland, M. Käll, G.W. Bryant, and F.J. García de Abajo, Optical properties of gold nanorings, *Phys. Rev. Lett.* **90**, 057401 (2003).
- (2) H. Xu and M. Käll, Surface Plasmon Enhanced Optical Forces in Silver Nanoaggregates, *Phys. Rev. Lett.* **89**, 246802 (2002).
- (3) H. Xu, E.J. Bjerneld, M. Käll, and L. Börjesson, "Spectroscopy of Single Hemoglobin Molecules by Surface Enhanced Raman Scattering", *Phys. Rev. Lett.* **83**, 4357 (1999).

Semiconducting nanostructures obtained by self-assembling processes

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The solid-state properties of organic electronic materials are determined not only by those of individual molecules but also by those of ensembles of molecules. The ability to control the supramolecular architectures is thus essential in optimising the properties of conjugated materials for their use in “supramolecular electronics”; this is primordial for technological applications in nanoelectronics. For instance, a clear correlation between the molecular structures, the mesoscopic structures, and the optical properties has been recently established (1). Self-assembly of synthetic materials such as thiophene-, paraphenylene-, and fluorene-based oligomers and polymers, has been proposed as a means of fabrication of nano-devices.

Here, we report on the observation by atomic force microscopy (AFM) of 1D and 2D nanoscale architectures obtained in the solid-state from solutions of molecularly-dissolved conjugated materials, and demonstrate that the conjugated molecules can organize onto a surface over lengthscales from nanometers to several microns, forming semiconducting fibrils by pi-stacking processes (2). The presence of bulky side chains or chiral centers are also drastically affecting the final morphology (3). It appears that the formation of unidimensional supramolecular organization (*i.e.*, fibrils) is predominant only when the molecular interactions are stronger than the molecule/surface interactions; otherwise, 2D-morphologies dominate. These facts strongly suggest that the nature of the surface is one key parameter governing the formation of the supramolecular assemblies.

References:

- (1) Grimsdale, A.C., Leclère, Ph., Lazzaroni, R., Mackenzie, J. D., Murphy, C., Setayesh, S., Silva, C., Friend, R. H., and Müllen, K. Correlation between Molecular Structure, Microscopic Morphology and Optical Properties of Poly(tetraalkylindenofluorene)s, *Adv. Funct. Mater.*, **12**, 729-733 (2002).
- (2) Leclère, Ph., Hennebicq, E., Calderone, A., Brocorens, P. Grimsdale, A.C. Müllen, K. Brédas, J.L. and Lazzaroni, R. Supramolecular Organization in Block Copolymers with a Conjugated Segment: A Joint AFM/Molecular Modeling Study, *Prog. Polym. Sci.*, **28**, 55-81 (2003).
- (3) Schenning, A.P.H.J., Kilbinger, A.F.M., Biscarini, F., Cavallini, M. Cooper, H.J. Derrick, P.J. Feast, W.J., Lazzaroni, R., Leclère, Ph., McDonnell, L.A., Meijer, E.W., Meskers, S.C.J. *Supramolecular Organization of a,a'-Disubstituted Sexithiophenes*, *J. Am. Chem. Soc.*, **124**, 1269-1275 (2002).

DUAL-FUNCTION MOLECULAR MATERIALS: DESIGN OF CONDUCTING FERROMAGNETS

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One of the most appealing aims in the field of molecular materials is to create multifunctional solids. An attractive approach to this issue is to make two-network hybrids from distinct molecules able to bring different physical properties to the material. Such strategy has been very successful in the preparation of crystalline solids that exhibit coexistence of electrical conductivity and magnetism,¹ as in the first molecular ferromagnetic metal (BEDT-TTF)₃[MnCr(ox)₃],² formed by alternating self-assembled monolayers of a bimetallic polymeric oxalate complex and of an organic radical. These multilayers are 0.36 and 1.3 nm thick, respectively, and are responsible for the appearance of ferromagnetic ordering and metal-like conductivity, that coexist down to 0.3 K.

Here we will present our more recent results in this area, where we have made use of the advantages of molecular chemistry to prepare a whole family of multilayered (ferro)magnetic conductors of general formula (TTFs)_x[M^{II}M^{III}(ox)₃].(CH₂Cl₂) [TTFs = tetrathiafulvalene derivative; M^{II}= Mn, Co; M^{III} = Cr, Rh; 2.5 < x < 3]. These studies have allowed us to obtain important correlations between physical properties and crystal structure, and therefore to control the physical properties of the products by modification and design of the starting molecular building blocks.

References:

- (1) Day, P. & Coronado, E. Molecular materials combining magnetic and conducting properties. In: Miller, J.S. & Drillon, M. (Eds.) *Magnetism: Molecules to materials* **Vol. 4** (Wiley-VCH, 2003).
- (2) Coronado, E. et al. Coexistence of ferromagnetism and metallic conductivity in a molecule-based layered compound. *Nature*, **408**, 447-449 (2000).

Catalytic Rotaxanes; Mimicking Nature's Processive Catalysts

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Chirality is one of the key tools used by nature to construct functional assemblies. In the past years I have worked on a programme to investigate how chirality, in particular helicity can be expressed in a hierarchical fashion to generate large helical nano-sized structures.¹ I will focus in particular on our recent work in the construction of chiral functional nano-objects based upon helical polyisocyanides. These rigid polymers are formed by the spontaneous stereoselective polymerisation of alanine-alanine isocyanides. The resulting nanorods are stiffer than DNA, due to a beta-sheet-like array of the side-chains along the polymer backbone.² In the case of the porphyrin derivative, single molecule porphyrin nanowires with lengths of 300 nanometers are formed, in which the excited-state is delocalized along the wire.³ More recently micrometer long perylene nanowires have been synthesized and the single molecule photophysical properties studied by NSOM. In addition to the homopolymers more soluble block copolymers consisting of a poly(isocyano-alanyl-thiophene) block and a polystyrene block were observed to self-assemble in water to give stable vesicular architectures, which upon cross-linking form conducting nano-vesicles. Inclusion of enzymes within these chiral vesicles results in the construction of a unique type of stereo-selective nanoreactor.⁴ The development of these novel nano-objects, their properties and their applications will be discussed

References:

- (1) **A.E. Rowan** and R.J.M. Nolte, Helical Molecular Programming, *Angew. Chem. Int. Ed. Engl.* **37**, 63-67 (1998).
- (2) Cornelissen, J.L.L.M. Donner, R.De. Gelder, W. Sander Graswinckel, G.A. Metslaar, **A.E. Rowan**, N.A.J.M. Sommerdijk, R.J.M. Nolte 'β-Helical Polymers from Isocyanopeptides,' *Science* 293, 676-680, (2001).
- (3) Witte, P.A.J.W.; Castricaino, M., Corneliessen J.J.L.M., Monsu Scolaro, L., Nolte R.J.M., Rowan, A.E. 'Helical Polymer-Anchored Porphyrin Nanorods', *Chem. Eur. J.* **9**, (2003).
- (4) Vriezema, D.M. Hoogboom, J., Velonia, K., Takazawa, K., Christianen, P.C.M., Maan, J.C., **Rowan, A.E.**, Nolte, R.J.M. 'Vesicles and polymerized vesicles from thiophene containing rod-coil block copolymers' *Angew. Chem. Int. Ed. Engl.* (2003)

Electrophoretic migration of DNA in lyotropic liquid crystals.

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Lyotropic liquid crystals form highly regular porous matrices with aqueous channels on the nanometer length scale. We have used the cubic phases formed with water by either an amphiphilic blockcopolymer (Pluronic F127) or by a lipid (monoolein) for electrophoretic separation of DNA. Our goal is to use the well-defined pores and the amphiphilic environment to obtain new separation motifs compared to conventional matrices, and the phase diagrams to optimise applications. The Pluronic crystal consists of close-packed micelles and its main advantage is that the cubic phase melts below 10°C. Hence the separated biomolecules can be recovered in a biologically active state in preparative applications. The monoolein crystal is bicontinuous, and a main advantage is that it is in equilibrium with a water-rich phase. This phase-behaviour can be exploited in the useful sub-marine mode of analytical electrophoresis. In the Pluronic system electrophoretic migration of double-stranded DNA does not occur in the cubic crystal lattice, but most likely along grain-boundaries in the polycrystalline samples. The migration of single-stranded DNA in the monoolein is retarded compared to free solution and conventional gels, to an extent which is consistent with migration through the nm-pores.

Hybrids of metal nanoparticles with highly branched amphiphilic macromolecules. Synthesis, properties and potential applications

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Transition metal clusters and colloids with particle sizes in the range of one to ten nanometers are of widespread interest.¹ Thermodynamically favored aggregation is usually suppressed by adsorption of low-molecular-weight surfactants or polar linear polymers on the nanoparticle surface. More recently, motivated by the concept of particle size control by means of synthesis in a confined environment^{1b,c} and the challenge of efficient nanoparticle stabilization, hybrids of dendrimers with metal nanoparticles have been investigated. By contrast to perfectly branched monodisperse dendrimers, readily accessible hyperbranched polymers possess a randomly branched topology.

Amphiphilic modification of hyperbranched polyglycerol² or polyethyleneimine^{3c} by partial esterification resp. amidation with fatty acids results in macromolecules with an apolar shell and a polar core. Metal nanoparticles are stabilized efficiently by these materials, the polar moieties being responsible for adsorption to the particle surface and the apolar region conveying solubility also in apolar organic solvents.³ Such soluble polymer/palladium nanoparticle hybrids are catalytically active for e.g. hydrogenation reactions. The catalyst can be recovered by ultrafiltration, also in a continuous fashion.^{3a,b,d} Hybrids of amphiphilic polyethyleneimine with silver particles form antimicrobial surface coatings.^{3c}

References:

- (1) a) *Clusters and Colloids: From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, 1994, p. 459-544. b) M. Antonietti, E. Wenz, L. Bronstein, M. Seregina, *Adv. Mater.* **1995**, 7, 1000-5. c) J. P. Spatz, A. Röscher, M. Möller, *Adv. Mater.* **1996**, 8, 337-40.
- (2) A. Sunder, M. Krämer, R. Hanselmann, R. Mülhaupt, H. Frey, *Angew. Chem. Int. Ed. Engl.* **1999**, 38, 3552-4; *Angew. Chem.* 1999, 38, 3758-61.
- (3) a) S. Mecking, R. Thomann, H. Frey, A. Sunder, *Macromolecules* **2000**, 33, 3958-60. b) S. Mecking, U. Schlotterbeck, R. Thomann, M. Soddemann, M. Stieger, W. Richtering, H. Kautz, *Polym. Mat. Sci. Eng.* **2001**, 84, 511-2. c) C. Aymonier, U. Schlotterbeck, L. Antonietti, P. Zacharias, R. Thomann, J. C. Tiller, S. Mecking, *Chem. Commun.* **2002**, 3018-9. d) R. Sablong, U. Schlotterbeck, D. Vogt, S. Mecking, *Adv. Synth. Catal.* **2003**, 345, in press.

MD simulations of a [2]catenane-based molecular switch

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So-called “molecular” machines represent an appealing alternative to the construction of devices, being based on a „bottom-up“ approach, in contrast with the usual miniaturization technology. In particular, bistable molecular switching devices can be built up by exploiting changes in electronic properties induced by conformational rearrangements. In this work we investigated, by means of theoretical calculations, the conformational rearrangement mechanism taking place on a [2]catenane molecule. Recently it has been shown that it is possible to build up solid state [2]catenane-based molecular switches by exploiting the circumrotational motion of one molecular ring with respect to the other one upon oxidation and reduction. We focused on the reaction mechanism and studied the conformational rearrangement and the electronic properties related to this phenomenon. Force-field based molecular dynamics techniques were adopted for the description of conformational changes, in conjunction with a hybrid QM/MM approach for the description of the electronic properties. In particular, a recently introduced approach based on an action-derived molecular dynamics in the study of rare events was applied.

Synthesis and photochemical properties of a [2]-catenane constructed around a $\text{Ru}(\text{Diimine})_3^{2+}$ complex used as a template

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A [2]catenane has been constructed using an octahedral complex of the $\text{Ru}(\text{diimine})_3^{2+}$ family as a scaffold. Two diimine chelates have been incorporated in a ring prior to the ruthenium(II) complexation reaction. The macrocyclic complex thus obtained has been subsequently threaded by a long linear fragment containing the third chelate. The ruthenium(II)-complexed catenane, cyclized by ring closing metathesis, is the first example of an interlocking ring system built around an octahedral tris-chelate complex.

Its photochemical properties, in relation to light-driven molecular machines will be also discussed. The photochemical studies, show that the bipy-incorporating ring is cleanly decoordinated under the action of light, in the presence of Et_4Cl , leading to a catenane for which the two rings are only mechanically linked.

Spin-crossover complexes: Towards molecular electronic devices

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The spin-crossover phenomenon is one of the most spectacular examples of molecular bistability. Spin-crossover complexes, displaying thermo-, photo-, magneto- and piezo-chromic properties, are of high potentiality in the area of multifunctional materials, especially for applications in memory and display devices and as molecular switches [1]. In this communication we present our results for addressing these materials by short thermal, magnetic (30T) or pressure (2 kbar) pulses in the thermal and piezo-hysteresis interval. Beside the well-known optical and magnetic methods, a novel electric means for reading the stored information at a microscopic level has been discovered and will be presented for the first time [2]. Finally, the important question of size reduction (i.e. micro/nano-structuration) effects on the physical properties as well as the relevance of the Raman microscopy technique for observation of spin-transitions with high spatial resolution will be discussed [3].

References:

- [1] Kahn, O.; Martinez, C.J. Spin-transition polymers: From molecular materials towards memory devices, *Science* **279**, 44 (1998)
- [2] Bousseksou, A.; Demont, P.; Menegotto, G.; Molnar, G.; Tuchagues, J.P.; Bonnet, J.J. Observation of a thermal hysteresis loop in the dielectric constant of spin-crossover complexes: Towards molecular memory devices, *Appl. Phys. Lett.* (submitted)
- [3] Molnar, G.; Zwick, A.; Bousseksou, A.; McGarvey, J.J. The spin-crossover phenomenon in the solid state: Do domains play a role? A micro-Raman study, *Chem. Phys. Lett.* **367**, 593 (2003)

Alkyl resorcinarenes and pyrogallarenes as structural subunits for self-organising molecular assemblies

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Resorcinarenes have proven to be fruitful starting compounds for complexation and crystal engineering purposes due to their prosperous properties such as hydrogen bonding to upper rim, π basic cavity capable to include small guests and hydrophobic interactions with lower rim functionalities.¹

Our current studies have concentrated on complexation and encapsulation of small alkyl ammonium cations by alkyl resorcinarenes.^{2,3} We have learned that resorcinarenes willingly encapsulate small ammonium cations in solid state, in solution and in gas phase. However, in crystalline state solvent plays a key role in capsule formation, since the capsule forming resorcinarenes are held together by hydrogen bond bridges via solvent molecules.

A striking difference in capsule types is observed when an additional hydroxyl group is added to upper rim of the host by using pyrogallol as a starting compound instead of resorcinol. Pyrogallarenes form directly hydrogen bonded capsules, i.e. no solvent is needed to mediate the capsulation. Also an interesting heteroconformational capsule was observed to form even without the presence of ammonium guests.

In the synthesis of ethyl pyrogall[4]arene a novel hexameric ethyl pyrogall[6]arene was observed to form as a side product. The studies to possibly utilise the pyrogall[6]arene as a starting compound for further synthesis and complexation studies are currently underway.

References:

- (1) Timmerman, P., Verboom, W. & Reinhoudt, D. N., Resorcinarenes. *Tetrahedron*, **52**, 2663-2704 (1996).
- (2) Mansikkamäki, H., Nissinen, M. & Rissanen K., Encapsulation of diquats by resorcinarenes: a novel staggered anion-solvent mediated hydrogen bonded capsule. *Chem. Commun.*, 1902-1903 (2002).
- (3) Mansikkamäki, H., Nissinen, M., Schalley, C. & Rissanen, K., Self-assembling Resorcinarene Capsules: Solid and Gas Phase Studies on Encapsulation of Small Alkyl Ammonium Cations. *New J. Chem.*, **26**, 88 – 97 (2003).

The Coordination Chemistry of Carbon Nanotubes: a Density Functional Study through a Cluster Model Approach

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The unique miniature structure of carbon nanotubes, together with their remarkable electronic properties, renders them ideal candidates for their exploitation in the production of molecular scale machines and nanoelectronic devices. Although several potential applications have been proposed, it comes out that chemical modification will be conclusive to foster some applications of carbon nanotubes. The covalent attachment of appropriate moieties on the nanotubes sidewalls can improve their solubility and ease of dispersion and can allow their chemical anchorage onto surfaces and polymer matrixes. The organometallic chemistry of carbon nanotubes is still a relatively unexplored area, and only recently Banerjee and Wong reported the functionalization of the nanotubes sidewalls with the Vaska's complex (*Nanoletters*, 2, 49, 2002) and with the Wilkinson's catalysts (*J. Am. Chem. Soc.*, 124, 8940, 2002). It has been showed that the covalent functionalization with transition metals complexes make carbon nanotubes soluble and stable in organic solution, allowing their further manipulation and their utilization in homogeneous catalysis. Moreover, the coordination with transition metals provides means of tuning the electronic and mechanical properties of carbon nanotubes in a controllable manner. Accurate theoretical investigations on functionalized carbon nanotubes may help to clarify the effects of chemical modifications on the electronic and structural properties. Density Functional Calculations at a non local level have been performed to analyze the interaction of transition metal complexes with carbon nanotubes, adopting clusters of finite size as models, that allow to reproduce the essential features of the electronic interactions. Polycyclic aromatic hydrocarbons, resembling the honeycomb lattice topology of nanotubes, have been used to modelize the nanotube surface and suitable geometric constraints have been imposed to reproduce the curvature of the nanotube surface. Geometry optimizations have been performed under these constraints, pointing out the most favourable coordination sites for the metal fragment on the carbon atoms surface and the electronic properties of the resulting systems.

References:

- (1) Carbon Nanotubes
- (2) Functionalization
- (3) Density Functional Theory

Hollow polymeric capsules covered with S-layers

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In the last ten years hollow capsules with defined walls made of polyelectrolyte layers (using the layer by layer technique) have been prepared and characterized (1). Crystalline bacterial cell surface layers (S-layers) are one of the most common outermost cell envelope components of the prokaryotic organism and represent the simplest biological membranes developed during evolution (2). In this work, we try to crystallize S-layers on the outer surface of microcapsules.

Zeta potential measurements show a slight variation in the potential value for three different types of S-layer deposit on polyelectrolyte covered particles. Comparing these results with the zeta potential for particles without protein, we arrive at the conclusion that they are covered by the S-layer.

TEM micrographs, fluorescence microscopy and laser scanning confocal microscopy experiments on capsules were carried out. They show that different isolated S-layers crystallize on hollow capsules, preferably on negative ones (PSS as outer layer). Adsorption of protein occurs for positive capsules too (PAH as outer layer), however the crucial question about the structure remains. AFM studies on solid support lead to similar conclusions.

Experiments with capsules coated with secondary cell wall polymers and S-layers are presented. S-layers rearrange due to specific interactions (sugar-protein) with the secondary cell wall polymer.

References:

- (1) Möhwald, H. From Langmuir monolayers to nanocapsules. *Colloid Surf. A* **171**, 25-31 (2000).
- (2) Sleytr, U. B., Messner, P., Pum, D., Sára, M. Crystalline bacterial cell surface layers (S-layers): From supramolecular cell structure to biomimetics and nanotechnology. *Angew. Chemie Int. Ed.* **38**, 1034-1054 (1999).

Photochromic and chromogenic supramolecular switches

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At Exeter, we are interested in the development of functional photo-active supramolecular receptors, where the complexation of a guest species can affect and control the photochromic¹ or chromogenic² response of the system. Each photochromic compound is designed to contain at least one anthracene group. Upon photoirradiation, two anthracene units reversibly dimerise in solution, either in an intra- or an inter-molecular fashion, to form symmetrical cycloadducts. A large conformational change is thus brought about which drastically affects the binding affinity towards guests. However the presence of a guest species can also affect the efficiency and rate of the forward and reverse processes, allowing a particular photochromic state to be ‘locked’ or ‘unlocked’ by complexation.³ We will describe our recent work in this area and also our current efforts at preparing anthracene-tagged oligonucleotides for the development of photochromic DNA sensors. We have also developed a chromogenic switch in the form of a ferrocene-containing receptor that can bind both cations and anions.² Complexation of anions (F⁻) brings about an observable colour change in acetonitrile solution at sub-millimolar concentrations; however the addition of cations (K⁺) switches the colour off.

References:

- (1) McSkimming, G., Tucker, J. H. R., Bouas-Laurent, H., Desvergne, J. P., Coles, S. J., Hursthouse, M. B. & Light, M. E. Photoinduced formation of a cryptand from a crown ether; an unexpected switch in cation binding affinity. *Chem. Eur. J.* **8**, 3331–3342 (2002).
- (2) Miyaji, H., Collinson, S. R., Prokes, I., & Tucker, J. H. R. A ditopic ferrocene receptor for anions and cations that functions as a chromogenic molecular switch. *Chem. Commun.* 64–65 (2003).

Reorientation in block copolymer melts as detected on-line via FT-Rheology and external 2D-SAXS

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The application of oscillatory shear strain with a frequency $\omega_1/2\pi$ results in the non-linear regime not only in a phase shift but also in contributions with higher frequencies: $3\omega_1$, $5\omega_1$, $7\omega_1$ and so forth within the torque response. These mechanical contributions can be analyzed in Fourier space as spectra [1, 2]. A feature article about this method can be found in [2].

This analysis was applied to the oscillatory shear of a PS-PI diblock copolymer melt below the order disorder transition temperature T_{ODT} [3]. The kinetics of the shear induced macroscopic shear orientation process of an macroscopically unoriented sample was determined via the intensities $I(3\omega_1)$ and the variation in time of the non-linear response. In the here presented work, the block copolymer was first preoriented to reach a defined macroscopic orientation (parallel) and afterwards the shear frequency was increased to reach a macroscopically perpendicular regime (see Fig. 1). The preorientation was conducted within 10 h, the final orientation was reached after additional 10 h shear after switching the frequency to 2 Hz. The time evolution of this process was followed on-line by FT-Rheology and off-line by 2D-SAXS measurements. The X-ray analysis was conducted at times where FT-Rheology indicated major changes.

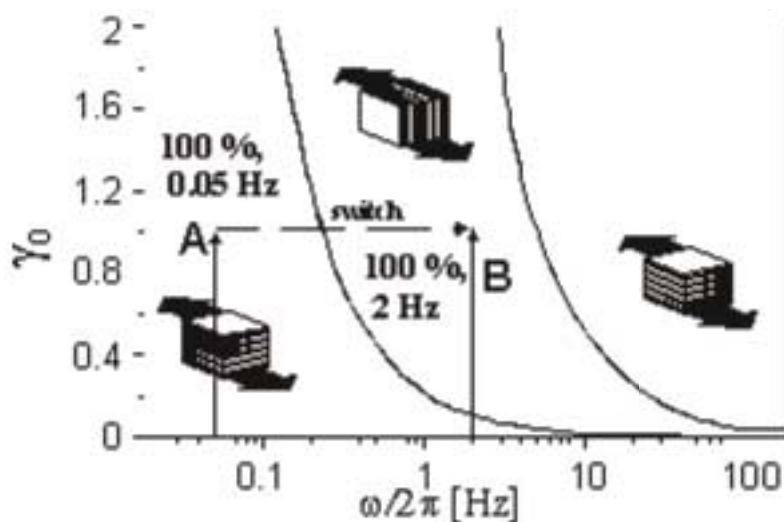


Fig. 1 Basic idea of the shear experiment conducted on a block copolymer.

References:

- (1) M. Wilhelm, P. Reinheimer, M. Ortseifer; High Sensitivity Fourier-Transform Rheology; *Rheol. Acta* **38** (1999) 349
- (2) M. Wilhelm; FT-Rheology (feature article); *Macromol. Mater. Eng.* **287** (2002) 83
- (3) M. Langela, M. Wilhelm, U. Wiesner, H.W. Spiess; Microphase reorientation in block copolymer melts as detected via FT-Rheology and 2D-SAXS; *Macromolecules* **35** (2002) 3198

Forces in and between self-assembled monolayer structures

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Self-assembly-processes are driven by intermolecular and interparticle forces. While certain components of the total interaction between particles can be manipulated to achieve a particular interaction, specificity or organization, all components of interparticle interactions cannot be controlled independently. With particular emphasis on organically modified metal structures, this presentation will highlight some aspects of dispersion forces, wetting behaviour and monolayer properties, and the relevance of these phenomena to interparticle interactions will be illustrated with both experimental and computational results for range of systems interacting in aqueous media.

Nanoscience and nanotechnology by self-organization

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Supramolecular chemistry aims at constructing highly complex chemical systems and advanced materials by designing arrays of components held together by intermolecular forces. The implementation of molecular recognition and information offers means for controlling the evolution and the architecture of supramolecular entities as well as of organized phases as they spontaneously build up from their components through self-organization.

Supramolecular chemistry is also intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their constituents. The same holds for molecular chemistry when a molecular entity contains covalent bonds that may form and break reversibly, so as to make possible a continuous change in constitution and structure by reorganization and exchange of building blocks. These features define a *constitutional dynamic chemistry* that allows for self-organization on both the molecular and supramolecular levels.

The design of molecular information controlled, “programmed” and functional self-organizing systems provides an original approach to nanoscience and nanotechnology. The spontaneous but controlled generation of well-defined, functional molecular and supramolecular architectures of nanometric size through self-organization represents a means of performing programmed *engineering* and *processing* of *functional nanostructures*. It offers a very powerful alternative to nanofabrication and to nanomanipulation for the development of nanotechnology.

Implementations in the generation of functional organic and inorganic architectures will be presented.

References:

Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH Weinheim, **1995**.

Lehn, J.-M., “*Supramolecular Chemistry/Science – Some Conjectures and Perspectives*”, in *Supramolecular Chemistry: Where It Is and Where It Is Going* (R. Ungaro, E. Dalcanale, eds.), Kluwer, Dordrecht, **1999**, pp. 287-304.

Lehn, J.-M., “*Toward complex matter : Supramolecular chemistry and self-organization*”, Proc. Natl. Acad. Sci. USA, **2002**, *99*, 4763.

Lehn, J.-M., “*Toward self-organization and complex matter*”, Science, **2002**, *295*, 2400.

Life-Like Nanotechnology: Soft-Matter Nanofluidic Devices by Self-Assembly & Self-Organization.

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Methods are presented for the construction of fluid state lipid bilayer networks of high geometrical and topological complexity consisting of surface-immobilized unilamellar vesicles (~5-25 μm in diameter) conjugated with nanotubes 50-150 nm in radius. Within networks, self-organizing branching nanotube architectures were produced. Formation of branching nanotube networks appears to follow a minimum-bending energy algorithm that solves for pathway-minimization.

The membrane composition (*e.g.* lipids, transporters, receptors, and catalytic sites) and container contents (*e.g.* catalytic particles, organelles, and reactants) can be controlled on the single-container level allowing complex chemical programming of networks. Fluid movement in nanotubes and materials exchange between conjugated containers can be obtained by using a moving boundary or by transport of vesicles integrated with the nanotube wall. In both instances, transport is modulated by changes in membrane tension. Thus, networks of nanotubes and vesicles serve as a platform to build nanofluidic devices operating with single molecules and particles and offers new opportunities to study chemistry in confined biomimetic compartments. The networks can also be used to build nanoscale chemical laboratories for applications in analytical devices as well as to construct computational and complex sensor systems that also can be integrated to living cells.

References:

- (1) R. Karlsson, A. Karlsson, M. Karlsson, A-S Cans, M. Voinova, J. Bergenholtz, A. G. Ewing, B. Åkerman, O. Orwar. Moving-wall-driven flows in nanofluidic devices. *Langmuir*, (2002) **18**, 4186-4190
- (2) M. Karlsson, K. Sott, M. Davidson, P. Linderholm, A-S Cans, O. Orwar. Formation of Geometrically Complex Lipid Nanotube-Vesicle Networks of Higher Order Topologies. *PNAS*, (2002) **9**, 11573-11578
- (3) A. Karlsson, M. Karlsson, R. Karlsson, A-S. Cans, Anette Strömberg, Frida Ryttsén, O. Orwar. Networks of nanotubes and containers *Nature*, (2001) **409**, 150-152
- (4) M. Karlsson, K. Sott, A-S. Cans, R. Karlsson, A. Karlsson, O. Orwar. Micropipet-assisted formation of microscopic networks of unilamellar lipid bilayer nanotubes and containers. *Langmuir*, (2001) **17**, 6754-6758.
- (5) M. Karlsson, K. Sott, M. Davidson, P. Linderholm, A-S Cans, O. Orwar. Formation of Geometrically Complex Lipid Nanotube-Vesicle Networks of Higher Order Topologies. *PNAS*, (2002) **99**, 11573-11578

NOVEL σ -CONJUGATED WIRES: A QUANTUM CHEMICAL STUDY OF THEIR STABILITIES AND CHARGE TRANSPORT ABILITIES

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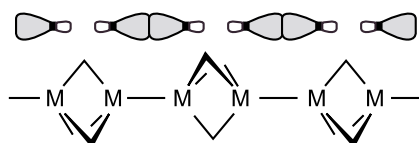
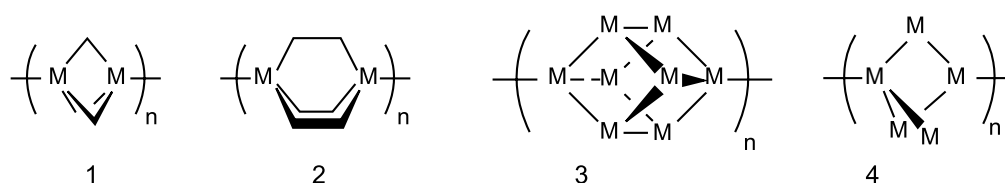
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Linear polysilanes and polystannanes are σ -conjugated compounds.¹ However, they are less suited as molecular wires for charge transport because they are conformationally flexible and conducting electrons and holes are easily trapped.² We instead propose σ -conjugated wires that are oligomers of compounds **1** – **4**. These wires would be rigid and their band gaps could be tuned by choice of Group 14 element M. In oligomers of **1** and **2** the conjugation stems from through-space interaction between the bridgehead atoms M, and their band gaps can also be varied by the M–M distance.

M = Si, Ge, or Sn (substituents in 3 and 4 omitted for clarity)



Properties of the monomers and oligomers of **1** – **4** have been probed by ab initio and DFT computations. Results on the static dipole polarizabilities of the oligomers, as well as charge transfer along the backbone of cationic and anionic oligomers will be presented. Monomers **2** – **4** have been synthesized before, and our calculations now reveal that the strain of **1** decreases as one goes from M = C to M = Sn. Since the all-carbon oligomers of **1** are stable at ambient conditions, we reason that also the heavier oligomers of **1** are realizable synthetic targets.

References:

- (1) Miller, R.D. & Michl, J., Polysilane high polymers *Chem. Rev.* **89**, 1359-1410 (1989).
- (2) Ichikawa, T., Yamada, Y., Kumagai, J. & Fujiki, M., Suppression of the Anderson localization of charge carriers on polysilane quantum wire, *Chem. Phys. Lett.* **306**, 275 – 279 (1999).

Monolayer protected clusters as tunable multi-valent redox species

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Solutions of thiol protected gold nanoparticles, so-called monolayer-protected clusters (MPCs) can be used as multivalent redox mediators in electrochemical experiments due to their quantized double-layer charging properties¹. Their use in scanning electrochemical microscopy (SECM) experiments wherein the species of interest is generated at the tip electrode provides a simple means to adjust the driving force of the electron transfer (ET) reaction². Approach curves (tip current I vs. distance d from the substrate) obtained to perfectly insulating and conducting substrates indicate that MPCs can be used as conventional SECM redox mediators. Heterogeneous ET between MPCs in 1,2-dichloroethane and an aqueous redox couple (Ce(IV) , $\text{Fe(CN)}_6^{3-/4-}$, $\text{Ru(NH}_3)_6^{3+}$ and Ru(CN)_6^{4-}) was probed with both feedback and potentiometric mode of SECM operation. Depending on the charge-state of the MPCs, they can be accept/donate charge heterogeneously at the liquid/liquid interface. However, this reaction is very slow in contrast to ET involving MPCs at the metal/electrolyte interface².

The use of SECM together with the modification of the nanoparticle properties via changing the nature of the protecting layer forms a powerful combination to spatially resolved electrochemical detection with chemically tunable redox mediators.

References:

- (1) Templeton, A. C., Wueling, W. P. & Murray, R. W. Monolayer-Protected Cluster Molecules. *Acc. Chem. Res.* **33**, 27-36 (2000).
- (2) Quinn, B.M., Liljeroth, P. & Kontturi, K. Interfacial reactivity of monolayer protected clusters studied by scanning electrochemical microscopy. *J. Am. Chem. Soc.* **124**, 12915-12921 (2002).

Nanostructured Materials by Surfactant Self-Assembly and Solvothermal Synthesis

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Nanostructured materials may be prepared using self-assembled surfactant aggregates as structure directing agents. Both microemulsions and liquid crystalline phases are being exploited for this purpose. Also by employing solvothermal treatments metastable crystalline nanostructures can be synthesised at low temperatures. A method of preparing and macroscopically aligning nanometer-sized crystalline silver particles into millimeter long fibers was developed (1). The approach utilized the dual functionality of a reverse hexagonal liquid crystalline template containing a built-in reducing agent facing the aqueous domain. Slow formation kinetics allowed for efficient loading of the template and retained mesoscopic ordering. Titanium dioxide nanoparticles were prepared by hydrothermal treatment of reverse microemulsions containing different acids (2). The rutile phase formed when HCl was used, whereas HNO₃ gave anatase. Both phases catalyzed oxidation of phenol but via different reaction pathways. The rutile path was initially faster, but overall the anatase path was most rapid. A crystalline nanoporous narrow bandgap (250 meV) semiconductor with anisotropic electrical conductivity was synthesised by solvothermal treatment of mixtures of propylamine, KOH(aq), Sb and Te (3). The crystal chemical formula is $[K_{18}(H_2O)_{18}][Sb_{36}O_{54}Te_{36}]$ and it contains 9.0 Å Sb₁₂O₁₈ tubular units lined with potassium ions and water, and enclosed by unique 15.5 Å Te tubular units.

References:

- (1) Andersson, M., Alfredsson, V., Kjellin, P. & Palmqvist, A. E. C. Macroscopic alignment of silver nanoparticles in reverse hexagonal liquid crystalline templates. *Nano Lett.*, 2, 1403-1407 (2002).
- (2) Andersson, M., Österlund, L., Ljungström, S. & Palmqvist, A. E. C. Preparation of nanosize anatase and rutile TiO₂ by hydrothermal treatment of microemulsions and their activity for photocatalytic wet oxidation of phenol. *J. Phys. Chem. B.*, 106, 10674-10679 (2002).
- (3) Palmqvist, A. E. C., Iversen, B. B., Zanghellini, E., Behm, M. & Stucky, G. D. A crystalline nanoporous narrow bandgap semiconductor. *Angew. Chem. Int. Ed. Engl.* Submitted (2003).

Collective Magnetic Properties in Organization of Cobalt Nanocrystals

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Colloidal assemblies are used to synthesize magnetic cobalt nanocrystals [1]. Deposited on a substrate, this nanocrystals self assemble in 2D monolayers with local organization. Changing the nanocrystals concentration of deposited solution allows formation of mesoscopic quasi 3D film made of uncoalesced cobalt nanocrystals. Applying a magnetic field during the deposition process either parallel or perpendicular to the substrate, change the structure of the film made of nanocrystals [2]. Hence 1D chains, 2D monolayer, 3D thick film or stripes or organized dots can be obtained. Collective magnetic properties due to the dipolar interaction between adjacent nanocrystals in the mesostructure have been observed [3]. In the case of 1D linear chain a structural effect on the collective magnetic properties has been demonstrated. These results are confirmed by theoretical model.

References:

- [1]- 'Self -Organization of Magnetic Nanosized Cobalt Particles' C. Petit, A.Taleb and M.P. Pileni, *Advanced Materials*, 10, (1998), 259
- [2]- 'Three dimensional arrays of cobalt nanocrystals: Fabrication and magnetic properties' C. Petit, J. Legrand, V. Russier and M.P. Pileni; *J. Appl. Physics* 91, (2002), 1502
- [3] 'Collective Magnetic Properties of Cobalt Nanocrystals Self-Assembled in Hexagonal Network: Theoretical Model supported by Experiments" V. Russier, C.Petit, J. Legrand and M.P. Pileni; *Phys.Rev B* 62,(2000),3910

Toward Nanostructuring SAMS by X-Ray Irradiation inducing Specific Chemical Transformations: The first example of the chemical modification of an organic nitro thin film to an organic amine thin film by X-ray photoelectron irradiation on a SiO₂ surface

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The utilisation of high energy radiation as a nanowriting tools is receiving a great deal of attention. We have recently designed fullerene and triphenylene derivatives as high resolution resists¹ and passivated gold nanoparticles² that will be depassivated³ by an electron beam to fabricate high purity gold nanowires. Additionally, X-ray photoelectron spectroscopy (XPS) has been employed to investigate the chemical change in self-assembled films of 3-(4-nitrophenoxy)-propyltrimethoxysilane (NPPTMS) on silicon (Si/SiO₂) wafers upon XP irradiation. Organic films were prepared by immersing silicon substrates in NPPTMS solution for 2 hours, forming multilayer films with a thickness of 27 Å measured by ellipsometry. NPPTMS films were exposed to XP irradiation (Mg K at 1253.6 eV source) over a period of 447 minutes. Results from the XPS elemental composition data suggested chemical modification of the NO₂ group. As the time of irradiation increased the N (1s) binding energy at 405.6 eV decreased in intensity, whilst concomitantly the N (1s) binding energy at 399.6 eV appeared and increased in intensity over 447 minutes, suggesting conversion of NO₂ to NH₂. Although total nitrogen peak intensity (NO₂ and NH₂ regions) was found to decrease slightly upon continued irradiation (447 minutes), no significant changes were observed on O (1s), C (1s) and Si (2p) binding energy peaks. In order to confirm the conversion of NO₂ to NH₂, a self-assembled multilayer of NPPTMS on silicon was subjected to reductive conditions (SnCl₂/anhydrous EtOH) to chemically convert the NO₂ to the NH₂ group. The XPS of this chemically reduced multilayer film revealed that the binding energy of the N (1s) at 405.6 eV was not present, whilst the N (1s) binding energy at 399.6 eV was present. Thus, confirming our conclusion that NO₂ was reduced to NH₂ employing XP irradiation as a writing tool.

References:

- (1) 'Exposure Mechanisms of Fullerene Derivative Electron Beam Resists' A.P.G. Robinson, R.E. Palmer, T. Tada, T. Kanayama, E.J. Shelley, D. Philp, and J.A. Preece, *Chem. Phys. Lett*, **1999**, *312*, 369-374.
- (2) 'Dialkyl Sulfides: Novel Passivating Agents for Gold Nanoparticles' E.J. Shelley, D. Ryan, M. Couillard, D. Fitzmaurice, R.E. Palmer, P.D. Nellist, J.A. Preece, Y. Chen, *Langmuir*, **2002**, *18*, 1791-1795.
- (3) 'HREELS Studies of Gold Nanoparticles with Dialkyl Sulfide Ligands' Y. Chen, R.E. Palmer, E.J. Shelley, J.A. Preece, *Surface Science*, **2002**, *502/503*, 208-213.

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Molecularly Defined Rigid c(RGDfK) Nano-Templates Regulate Cell Adhesion by Control of $\alpha\beta3$ -Integrin Clustering

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The lack of high resolution bio-patterning methods has prevented direct examination of spatial size ranges that contribute to the process of cell adhesion to tissues or cells on a molecular scale. Studies of the structural arrangements of single ligand bound to integrins in cell membranes, i.e. integrin clustering, demand strict spatial control of cell adhesive areas which bind only one integrin receptor on the nanometer scale. We designed a hexagonally-close packed template for cyclic RGDfK [c(RGDfK)] peptides by self-assembly of diblock copolymers. Nanometer sized cell adhesive dots are positioned with high precision at 28, 58, 73 and 85 nm spacing in hexagonally-close packed patterns over extended glass cover slip areas. The adhesive dots are small enough (< 8 nm) that only a single $\alpha\beta3$ -integrin bind per dot exclusively. Thus, the template offers a unique rigid c(RGDfK) nanopattern to which only single $\alpha\beta3$ -integrin receptors can be arranged to obtain adhesion on these nanostructured interfaces. If adhesive dots are separated by more than 73 nm, cell attachment is constricted, as is cell spreading, formation of focal contact clusters, and actin stress fibre formation. Using microstructured nanopattern areas to allow for modulation of local ligand density on a micrometer lengthscale (second order structure), we demonstrated that this is not due to insufficient ligand density. Rather we attribute this cellular response to restricted $\alpha\beta3$ -integrin clustering. We found the maximum spacing at which adhesion restriction starts due to integrin clustering failure to be between 58 and 73 nm in MC3T3-Osteoblasts, B16-Melanocytes, and 3T3-Fibroblasts. Since the c(RGDfK) peptide is selective for $\alpha\beta3$ -integrin occupation, we propose that this length scale is universal in cells which may adhere via $\alpha\beta3$ -integrins.

Unconventional Nanofabrication

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Chemistry (with stimuli from biology and from macroscopic manufacturing), is beginning to develop a range of new concepts for fabrication of micro-and nanosystems: these include self-assembly, non-covalent synthesis, microprinting, micromolding, and microembossing. They also include photolithographic techniques--especially near-field techniques—derived from the tools used in these approaches. The objectives of this work are to be able to prototype microsystems rapidly, to fabricate 3D microsystems, to work with materials classes required from applications other than microelectronics, to lower costs and simplify processes required for certain types of microsystems, and to make nanostructures (defined as structures having < 100 nm features). Most of these techniques are focused on replication of masters rather than on creating masters (or masks), but both functions are served in some techniques.

These techniques--especially microprinting, micromolding, and microembossing--are subsumed in the phrase “soft lithography”. The adjective “soft” in this phrase refers to the elastomeric stamps or molds that are important in many of these techniques, and to the properties of organic materials in general.

This talk will outline progress in this area. The procedures, as currently developed, offer a series of new routes to nanostructures. They have not been applied to the fabrication of complex, multilevel electronically functional structures, but there are no physics-based barriers to this kind of application. Key practical problems are defect densities, distortions in the masks/stamps/molds in use, and registration in multilevel fabrication. The broad objective of this work is to open nanofabrication to chemists, biologists, and materials scientists who do not have ready access to the conventional technology of nanofabrication.

Synthesis and Characterization of Metallodendrimers With Potential Nonlinear Optical Applications

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Inorganic systems, such as polynuclear mixed valence complexes and metallodendrimers, have attracted significant attention due to their potential use in the new fields of molecular electronics and nanotechnologies. Although the search for new organometallic materials displaying nonlinear optical (NLO) properties is the focus of much current research activities, the synthesis and characterization of metallodendrimers for NLO applications has been far less studied. In particular, metal ions such as Ruthenium(II) are excellent templates for building 3D octopolar nonlinear optical metallodendrimers¹. Our previous results on the use of Ruthenium organometallic fragments with benzonitrile derivatives in the design and construction of new materials with enhanced NLO properties² prompted us to extend our work to the synthesis of metallodendrimers with this purpose³.

Herein we report the most relevant spectroscopic and structural results for a first generation of polynuclear Ruthenium(II) metallodendrimers. It was prepared by a divergent synthetic methodology, using the Ru(PP)₂Cl (PP= dppe, dpmm, (PMe₃)₂), Ru(η⁵-C₅H₅)(PP)₂ (PP= (PPh₃)₂, (PMe₃)₂) fragment and the 1,3,5-tricyanobenzene as a core. Aspects of the IR, UV-Vis, NMR spectra of the complexes are discussed. The electrochemistry of these complexes was also studied by cyclic voltammetry in order to get an insight on their reactivity and the electron richness of the metal centres.

References:

- (1) - **a)** Le Bosc, H., Le Boudier, T., Maury, O., Ledoux, I. & Zyss, J. Coordination chemistry for nonlinear optics: a powerful tool for the design of octopolar molecules and supramolecules. *J. Opt. A : Pure Appl. Opt.* **4**, S189-S196 (2002); **b)** Hurst, S. K., Cifuentes, M. P. & Humphrey, M.G. A rapid convergent approach to organometallic dendrimers: sterically controlled dendron synthesis. *Organometallics* **21**, 2353-2355 (2002) and references therein.
- (2) - **a)** Garcia, M. H., Rodrigues, J. C., Dias, A. R., Piedade, M. F. M., Duarte, M. T.; Robalo, M. P. & Lopes, N. Second harmonic generation of η⁵-monocyclopentadienyl ruthenium *p*-benzonitrile derivatives by Kurtz powder technique. crystal and molecular structure determinations of [Ru(η⁵-C₅H₅)((+)-DIOP)(*p*-NCC₆H₄NO₂)] [X], X=PF₆⁻, CF₃SO₃⁻ and [Ru(η⁵-C₅H₅)((+)-DIOP)(NCCH₃)] [PF₆]. *J. Organomet. Chem.* **632**, 133-144 (2001) and references therein.
- (3) - Freitas, F., Garcia, M. H., Mesquita, J. C., Piedade, M. F., Robalo, M. P. & Rodrigues, J. C. Synthesis of metallodendrimers for nonlinear optical applications, using the 1,2,3-tricyanobenzene (TCB) as a core. *Inorganic Chemistry-Euroconference on the Inorganic Side of Molecular Architecture*, San Feliu de Guixols, 31 August-5 de September, Spain, Abst. C3 (2002).

Supramolecular Chemistry Goes Gas Phase

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Due to the late development of soft ionization methods, mass spectrometry has long been applicable to weakly bound supramolecular species only to a very limited extent. Even with electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI), it is often difficult to conduct thorough studies of such complexes, because protic media (solvent of matrix) interfere with the non-covalent bonds. This is particularly true for hydrogen bonded systems.

The talk presents three examples, which illustrate how chemical problems beyond a mere mass determination can be addressed in supramolecular systems. First, structural questions can be answered by mass spectrometric means: Mass spectrometry allows to distinguish different topological isomers macrocyclic and catenated species. As a second example, mass spectrometry provides evidence for the container-like structure of dimeric, hydrogen bonded capsules with charged guests inside. First results on the barriers for guest release from these containers are discussed. The third example on self-assembling squares and triangles permits insight into the gas-phase reactivity of supramolecular complexes.

These examples illustrate the potential of mass spectrometry to unravel details of the structure, thermochemistry, and reactivity of supramolecular species.

References:

- (1) Schalley, C. A. Molecular Recognition and Supramolecular Chemistry in the Gas Phase, *Mass Spectrom. Rev.* **20**, 253 (2001).
- (2) Schalley, C.A., Müller, T., Linnartz, P., Witt, M., Schäfer, M. & Lützen, A. Mass Spectrometric Characterization and Gas Phase Chemistry of Self-Assembling Supramolecular Squares and Triangles, *Chem. Eur. J.* **8**, 3538 (2002).
- (3) Schalley, C.A., Martín, T., Obst, U. & Rebek, J. Jr. Characterization of Encapsulation Complexes in the Gas Phase and Solution, *J. Am. Chem. Soc.* **121**, 2133 (1999).

Micro and nano scale chemical analysis of individual subcellular compartments

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Although powerful imaging techniques exist for studying sub-cellular structures with nanometer resolutions, few techniques are available for elucidating the chemical contents of such sub-cellular architectures. We describe our efforts to develop an integrated platform based on single-molecule manipulation and detection together with micro and nano fluidics for characterizing the chemical compositions of nanometer-sized compartments within the cell, and to provide spatial information with regard to the intracellular localization and distribution of proteins and other biomolecules. This approach relies on the ability to generate, on demand, subpicoliter and subfemtoliter droplets inside micro- and nano- meter-sized channels, and on the use of such small droplets as reaction vessels for the chemical manipulation of single vesicles and other subcellular organelles. Once chemically tagged, the contained proteins and biomolecules are manipulated optically, then separated, and counted using single-molecule detection.

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Research Interests:

Development of synthetic routes to metal, metal oxide and metal chalcogenide nanosystems by Thermal and Plasma-CVD techniques and their thorough compositional, microstructural and morphological characterization by different analytical techniques. A major part of the research activity is devoted to the design and synthesis of suitable molecular precursors and to the investigation of their reactivity and decomposition patterns.

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Research Interests:

The overall aim of our research is the use of ligand design and coordination chemistry to synthesise coordination compounds which are tailored to mimic a specific structure or fulfil a specific function. We have research interests in three main areas: the synthesis of new magnetic materials; the synthesis of models for Non-Transferrin Bound Iron and the Synthesis and Characterisation of Luminescent Lanthanide Complexes.

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Research Interests:

Use of weak interactions in supramolecular chemistry for the conception of catanionic amphiphiles with biological activity. Correlation structure/aggregation/biological activity to improve the design of the drugs. Use of the self association behaviour of these amphiphiles for the targeted delivery of active substances.

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Research Interests:

Understanding chemical reactions at surfaces on a fundamental level. Specifically, the relationship between surface chemistry and morphology is investigated using ultrahigh vacuum surface science techniques. Metal nanoparticles deposited on oxide surfaces are used as model systems for understanding commercial heterogeneous catalysts, which typically consist of metal particles on an oxide support. The effects of particle size on the surface chemistry of the metal particles are being explored.

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Research Interests:

Combination of supramolecular chemistry and organic semiconductors with the aim to control the properties of plastic and supramolecular electronic devices.

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Research Interests:

Synthesis, supramolecular aspects and applications of subphthalocyanines (SubPcs). More specifically, I intend to develop new SubPcs and SubPc analogues assemblies (covalently and noncovalently-linked) in order to dramatically modify their physical properties and, in particular their nonlinear optical properties.

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Research Interests:

The focus of our research is the synthesis and use of defined polymers at interfaces. This includes interfaces of colloidal systems (solid/solid, solid/liquid, solid/vapor etc.) for the control of wetting, friction, adhesion, adsorption aggregation etc. as well as interfaces between chemistry, physics, biology and materials science.

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Research Interests:

*Oligothiophene molecular materials.
Electronic applications (field-effect transistors and light emitting diodes) of oligothiophenes or polyconjugated materials, in general.
Synthesis, electrochemistry and molecular spectroscopies (mainly infrared, Raman and UV-Vis-NIR) focused on the characterization of these class of molecules.
Quantum Chemistry directed towards the simulation and calculation of frontier orbitals, electronic properties and vibrational spectra of oligothiophenes as isolated identities and with solvent effects.*

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Research Interests:

Synthetic organic and polymer aspects of materials chemistry including the synthesis of functional polymers and nanoscopic materials, functionalized nanocrystals, directed assembly of nanoparticles, interfacial activity of polymers and particles, and synthetic polymers for medical applications.

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Research Interests:

Based on my study of Technical Chemistry I specialized in Biophysics. I did my diploma in the field of Electrophysiology where I investigated Ca^{2+} channels in living cells applying the Patch-Clamp technique. During my PhD work I am involved in studies on the mechanisms of protein-protein and protein-lipid interaction using atomic force microscopy (AFM) and surface plasmon resonance (SPR) as well as general techniques for the chemical modification of surfaces.

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Research Interests:

We are a molecular modeling and simulation group, and are interested in the structure, properties and applications of nanocomposite and nanoporous materials. The development of new realistic potential models and simulation methodologies aimed at these systems are important parts of our work, as is their efficient implementation on high-performance computers. We have related interests in both dynamic and equilibrium nanofluidic phenomena, including flows in nanometer-scale spaces and other capillary phenomena.

Dr. Zoran Konkoli

Condensed Matter Theory Group,
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Research interests:

reaction-diffusion systems, protein folding, macromolecular translocation, ab initio Quantum Chemistry (method development)

Dr. Rainer Haag

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Research Interests:

Dendritic Polymers as Highly Functional Polymeric Supports for Combinatorial Synthesis and Therapeutical Applications, Macromolecular Nanotransporters for DNA- and Drug-Delivery, Self-Assembled Monolayers (SAMs) for Bioactive Surfaces.

Dr. Johan Bergenholtz

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Research Interests:

Dynamics of colloidal dispersions, Rheology of complex fluids, Mode-coupling theory of glassy dynamics applied to colloids, Aggregation phenomena, Dynamics and transport in marginally stable colloidal systems.

Dr. Stefan Hecht

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Research Interests:

Our research program is engaged in the development of chemical approaches for future nanotechnology. Organic and polymer synthesis are utilized to generate various functional units and control their spatial orientation in order to create "smart" nanosized molecules as key components of tomorrow's materials. Our main focus is directed toward the design of organic nanotubes having defined dimensions and functionality. In addition, local manipulation and site-specific single molecule reactivity employing scanning probe techniques (in collaboration with physicists) as well as a variety of photoresponsive molecules are being investigated.

Dr. Fredrik Höök

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Research Interests:

My research is focused on novel sensing concepts at the micro- and nanoscale, allowing optimized detection of a broad range of biorecognition events. In particular, my research contribute with proof-of-concept platforms for protein identification from complex mixtures utilizing antibodies combined with biomimetic-inspired lipid-based surface templates, where proper handling of transmembrane proteins for functional analysis is also highly emphasized.

Dr. Mogens Brøndsted Nielsen

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Research Interests:

The research is centered on synthesis of new π -conjugated systems for materials and supramolecular chemistry. These systems are mainly based on the heterocyclic compound tetrathiafulvalene (TTF) that is a reversible two-electron donor. Acetylenic derivatives of TTF are targeted as molecular building blocks for acetylenic scaffolding in one and two dimensions.

Dr. Mats Lundberg

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Research interests:

Surfactant template synthesis of crystalline metal oxide materials with nanoporous structures (mesoporous materials). Electron microscopy techniques (SEM, TEM, STEM, cryo-TEM) with emphasis on high-resolution electron microscopy. Nanotechnology and materials science in general.

Prof. Kazuhiko Kinoshita

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Research Interests:

My research interests are focused on the synthesis and the studies of the physical properties of nanoparticles that may be metal, alloys or oxides. My research is devoted to fundamental aspects but also to the development of new applications like high density storage or gas sensors.

Dr. Christine D. Keating

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Research Interests:

We are broadly interested in structure-function relationships for supermolecular and superparticulate assemblies, and our efforts are strongly influenced by designs and mechanisms found in biology. Current research projects include (i) the use of DNA hybridization to assemble metallic nanowires at an aqueous-aqueous interface, (ii) aqueous phase formation within giant unilamellar vesicles for biomolecule microcompartmentation and cytomimetics, and (iii) optical characterization of segmented metallic nanowires as encoded supports for bioanalysis.

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Research Interests:

My research interests are located in the area of soft, i.e. organic and polymeric, surfaces and interfaces. In a team of currently 5 graduate students and 2 masters students, we study dynamic processes in confinement and constrained environments, such as phase transitions or chemical reactions in self-assembled monolayers (SAMs) or ultrathin polymer films, and explore avenues for nanofabrication of soft materials using scanning probe techniques under full environmental control. Our work also includes atomic force microscopy (AFM) - based single molecule force spectroscopy, chemical mapping of surfaces using functionalized AFM tips, polymer crystallization in ultrathin films and high velocity nanotribology. These projects are funded by MESA⁺ Research Institute of the UT, the Technology foundation STW, and the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) in the framework of a vernieuwingsimpuls project.

Dr. Harm-Anton Klok

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Research Interests:

The main objective of our work is to explore whether concepts that have been developed by Nature for the folding and organization of proteins can be integrated into materials science. In particular, we are interested in hybrid conjugates and block copolymers composed of a biologically-inspired peptide segment and a non-biological part and we investigate the question whether the ability of the peptide sequence to hierarchically self-organise into well-defined nanoscopic structures can be transferred to the hybrid molecules.

Dr. Mikael Käll

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Research Interests:

Theory and applications of surface plasmon resonances, in particular single molecule surface-enhanced Raman scattering (SERS).

Advanced bioimaging methods, in particular single molecule fluorescence techniques.

Optical spectroscopy of “exotic” oxides, such as CuO spin-ladders, manganites and high- T_c superconductors.

Dr. Philippe Leclere

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Research Interests:

Supramolecular organization of (conjugated) organic materials including oligomers, polymers, and block copolymers. Correlation between molecular architectures, mesoscopic structures and macroscopic properties of organic systems using scanning probe microscopy characterization.

Dr. Jose Galan Mascarros

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Research Interests:

In Molecular Magnetism: Synthesis, characterization and magnetic phenomena of single-molecule and molecule-based magnets.

In Multifunctional Materials: Synthesis and physical characterization of hybrid molecular materials exhibiting combination of electrical, optical and / or magnetic properties.

In Nanoscience: Preparation and characterization of functional organized nanostructured materials as nanoparticles and thin-films.

Dr. Alan Rowan

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Research Interests:

My research interests are primarily the construction of nano-sized functional architectures, utilizing the concepts of self-assembly. My current research topics include; catalytic molecular motors, enzyme cascades, liquid crystal displays, nanoelectronics and basic physical organic chemistry.

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Research Interests:

- 1) *Catalytic polymerization in aqueous emulsion as a novel route to submicron polymer particle dispersions.*
- 2) *Hybrides of highly branched amphiphilic macromolecules with nanoparticles, which can be catalytically or biologically active.*
- 3) *Polymer-bound soluble catalysts and their recycling.*

Dr. Francesco Mercuri

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Research Interests:

My research concerns the phenomenon of molecular bistability presented by spin-crossover, prussian blue analogue and other transition metal complexes. Using a variety of physical methods I study the mechanism of the piezo-, magneto-, thermo- and photo-induced switch between the two forms of the bistable compound. These phenomena are then modelled by means of two-level Ising like models. Finally, I am interested in the possible applications of these molecular materials for information storage and electronic devices at micro/nanosopic scale.

Dr. Maija Nissinen, Senior researcher

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Research Interests:

My research interest is single crystal X-ray crystallography of supramolecular compounds, especially host-guest complexes and weak interactions affecting the complexation. Currently the research is concentrated on the complexation properties of resorcinarenes and pyrogallarenes and in collaboration with Università La Sapienza, Rome the complexation properties of uranium containing ligands. Although the main interest is in the solid state studies, the supporting NMR titration and mass spectrometric studies as well as synthesis of novel host compounds are an important part of the research.

Dr. Francesca Nunzi

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Research Interests:

Theoretical investigations on the electronic structure and chemical properties of extended molecular systems, aggregate and clusters by means of ab initio (Hartree-Fock and post Hartree-Fock) methods, hybrid methods, and Density Functional Theory-based methods.

Research topic: *functionalization of fullerenes and carbon nanotubes by means of both organic both metal complexes for the development of nanostructured molecular devices.*

Dr. Jose Toca

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Research Interests:

We are interested in further development of this new type of “Biocapsules”, which should provide a template for future specific interactions and surface enzymatic reactions.

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Research Interests:

I am interested in functional supramolecular receptor systems; in particular those that are redox-active or photo-active. This allows for a redox or a photochromic process to control (or be controlled by) the complexation of a guest species. This approach can lead to the development of novel devices that can act as supramolecular switches or sensors.

Dr. Manfred Wilhelm

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Research Interests:

Method development in rheology, specifically non-linear methods under oscillatory shear “FT-Rheology” and the two dimensional extensions of FT-Rheology. Application of FT-Rheology to polymers, e.g. the influence of different topologies, e.g. long chain branching, and morphologies towards the non-linear mechanical response under large amplitude oscillatory shear.

A further topic is method development in Solid-State-NMR, especially with respect to dynamic and spatial heterogeneities in the 1 - 100 nm regime. More specifically: multidimensional exchange NMR and proton spin diffusion. Application of Solid-State-NMR to materials and questions of industrial relevance.

Dr. Thomas Ederth

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Research interests:

Self-assembly and functionalization of organic monomolecular films and amphiphilic bilayers. Molecular and lateral mesoscopic order in lipid bilayers; lipid rafts as functional devices. Structural characterization of surfactant bilayers in confined geometries and self-organized assemblies in multicomponent thin liquid films. Interfacial properties of water near hydrophobic surfaces.

Prof. Jean-Marie Lehn

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Research Interests:

My research interest is directed towards novel organic compounds with interesting electronic structures, and their applications in molecular electronics and spintronics. Focus is given to compounds based on the heavy Group 14 elements Si, Ge, and Sn. With a background in theoretical chemistry, I am interested in techniques for computations of properties of molecular wires and components, but also in synthetic techniques in Si, Ge and Sn chemistry. I also have an interest in Si=C bonded compounds and their applications to organic synthesis, and the synthetic knowledge gained from this project is crucial for realization of our molecular electronics components.

Dr. Bernadette Quinn

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Research Interests:

Electrochemical characterisation of monolayer protected clusters, lateral charge transfer in nanoparticle films, the influence of charge and protecting ligand on nanoparticle interfacial reactivity, liquid-liquid electrochemistry.

Dr. Anders Palmqvist

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Research Interests:

A general interest in synthesis, structural and spectroscopic characterisation of small particles, cage structures, micro- and mesoporous materials. More specific interest in synthesis of nanostructured materials by surfactant self-assembly and solvothermal synthesis. Main applications of interest are heterogeneous catalysis and thermoelectrics.

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Research Interests:

I am concerned by soft chemical synthesis of magnetic nanocrystals and their organization in mesoscopic structure. This new nanostructured materials present collective properties, which differ from that of the isolated nanocrystals and that of bulk materials. These organizations of magnetic nanocrystals could have numerous applications.

Dr. JA Preece

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Research Interests:

Current Research Interests of the Preece Nanoscale Research Laboratory: The design and synthesis of nanostructured materials is the focus of the research in the laboratory. However, collaboration with physicists, medics and engineers is allowing the investigation of these materials as nanoresists, gene delivery agents, and surface modifying materials.

Prof. Joachim Spatz

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Research Interests:

We develop non-conventional techniques for micro- and nanostructured surfaces. These are applied as tools for biomimetic investigations regarding cell adhesion, cell mechanics, and two-dimensional complex filament networks which are adaptive to external interferences. Research Areas: Nanolithography, Biofunctionalisation, Cell Biophysics, Biomimetic Concepts.

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Research Interests:

The recently formed Molecular Materials Research Group is part of the CQM - Centro de Química.

We seek to combine the methodologies of organometallic chemistry with those of coordination chemistry to prepare and characterise potentially useful molecular materials, namely dendritic(hyperbranched) and polymeric metal-containing systems, having in view their potential use as electronic and/or biomedical nanomaterials. Beyond the investigation of the electronic, electrochemical and optical properties of the materials we aim to understand how the chemical structure can control the molecular properties. Until the present, the two main projects of research are: Development of new organometallic dendrimers having in view their possible use as non-linear optical materials and the Synthesis of molecular wires.

Keywords: *organometallics, dendrimers, donor-acceptor systems, nonlinear optics, molecular wires, nanoelectronic materials.*

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Research Interests:

Supramolecular Chemistry, Molecular Recognition, Mass Spectrometry, Template Effects, Self-Organisation.

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Research Interests:

Our group is interested in developing methods in laser microscopy and spectroscopy as well as techniques of nanofabrication and microfluidics for applications in single-molecule studies, in the analyses of single cells and subcellular structures, and for understanding cellular biochemistry and function.

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