

CPP 1: Supramolecular Aggregates

Time: Monday 9:30–12:30

Location: H37

Invited Talk

CPP 1.1 Mon 9:30 H37
Dynamic Processes in Supramolecular Nanoassemblies —

•CHRISTIAN VON BORCZYKOWSKI — Center of nanostructured materials and analytics, TU Chemnitz, 09107 Chemnitz

Supramolecular aggregates of organic molecules have proven to be both biomimetic systems e. g. for photosynthetic reaction units and model systems for a development of model systems in bottom-up molecular electronic concepts. Due to that large range of properties such as functional groups and redox-potentials organic molecules are versatile building blocks blades of functionalized units. Complementary, semiconductor quantum dots of sizes in the nanometer range are in combination with quantum confinement tunable over a large range of broad band absorption combined with narrow band emission properties. This contribution will report the progress of the combination both of perspectives, namely chemical versatility of molecules and bandgap-tuning of semiconductor nanocrystals. Optical experiments on self-organized ensembles between dye molecules and CdSe nanocrystals will be in the center of this investigation. [1], [2].

[1] E. Zenkevich et al., J. Phys. Chem. B 109, 8679 (2005). [2] D. Kilin et al., J. Photochem. Photobiol. B (2006, in print).

CPP 1.2 Mon 10:00 H37

Controlled Fabrication of Molecular Nano-Dot Patterns —

•STEPHAN RATH, DIRK SAUER, and HELMUT PORT — 3. Physikalisches Institut, Universität Stuttgart

For applications in molecular electronics and photonics small dot-like structures are attractive objects as they can be individually addressed.

To fabricate nano-dots thin organic films are deposited at UHV conditions on helium-cooled substrates. Controlled annealing to room temperature transforms the films into homogeneous distributions of isolated dots by dewetting. This process can be quantified and optimized for different combinations of molecules and substrates.

To achieve regular and closely packed patterns of dots, we introduced topographically structured substrates as templates. In this way, we are able to control size, density and arrangement of nano-dots on mm²-sized areas. For characterization and single dot access two operation modes are applied: confocal microscopy in combination with AFM and scanning near-field optical microscopy (SNOM).

CPP 1.3 Mon 10:15 H37

The absorption spectrum of organic dye aggregates —

•ALEXANDER EISFELD and JOHN BRIGGS — Theoretische Quantendynamik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany

Certain molecular aggregates consisting of organic dyes are remarkable in exhibiting an intense and very narrow absorption peak, known as a J-band [1], which is red-shifted away from the region of monomer absorption. Apart from those dyes showing the J-band on aggregation, there are also dyes where the absorption maximum is shifted to higher energies. The width of the resulting absorption band (called an H-band) is comparable to that of the monomeric dyes and shows a complicated vibrational structure.

Following our analysis of the J-band [2,3] spectra of polymer aggregates using the CES approximation, a theory that includes vibrations explicitly, we show that the same approximation can account for measured H-band spectra. Using simple analytical forms of the monomer spectrum the origin of the widely-different shapes of H- and J-bands is explained within the CES approximation [4].

[1] T. Kobayashi, J-Aggregates. World Scientific, 1996

[2] A. Eisfeld, J. S. Briggs, Chem. Phys. 281, 61

[3] A. Eisfeld, J. S. Briggs, Phys. Rev. Lett. 96, 113003

[4] A. Eisfeld, J. S. Briggs, Chem. Phys. 324, 376

CPP 1.4 Mon 10:30 H37

Single molecule spectroscopy of dye - quantum dot

nanoassemblies on surfaces — •DANNY KOWERKO, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — Center of nanostructured materials and analytics, TU Chemnitz, 09107 Chemnitz

Nanoassemblies of semiconductor quantum dots (QDs) and organic molecules are promising objects of research and application in many fields of science and technology. Physics and chemistry of coupling mechanisms and possible interactions (i.e. energy transfer) are com-

plex and thus not yet fully understood. Förster resonance energy transfer has been proven to be one reason for quenching of CdSe QDs luminescence in the presence of pyridyl porphyrin molecules [1]. Already observed QD luminescence quenching in pyridyl functionalized perylenebisimide solutions promises such systems on a single molecule/single nanoparticle level. In order to be able to use such spectroscopic techniques even at cryogenic temperatures nanoassemblies need to be immobilized on surfaces. Here we report on the preparation and spectroscopic characterization of dye - QD assemblies on silica surfaces. We will show that there is clear evidence that such assemblies are formed in solution and are stable on the surface. [1] E. I. Zenkevich et al, J. Phys. Chem. B, 109, 8679, 2005.

15 min. break

CPP 1.5 Mon 11:00 H37

Selective mapping of the coordinate metal bonds in

supramolecular nanoarchitectures — •P. MÜLLER¹, M.S. ALAM¹, L.K. THOMPSON², U. KORTZ³, R. SAALFRANK⁴, M. RUBEN⁵, and J.-M. LEHN⁶ — ¹Physikalisches Institut III, Universität Erlangen-Nürnberg — ²Chemistry Department, Memorial University, St. Johns, Canada — ³School of Engineering and Science, International University, Bremen — ⁴Institut für Organische Chemie, Universität Erlangen-Nürnberg — ⁵Institut für Nanotechnologie, FZ Karlsruhe — ⁶ISIS, Université Louis Pasteur, Strasbourg, France

Coordinate-bonded 3d metal ions dominate the electronic density of states of organic molecules incorporating such metal centers. Supramolecular nanostructures of different structural complexity and incorporating different transition metal ions were investigated. The molecules were deposited from the solution onto HOPG surfaces. The structural and electronic properties were studied at the single-molecule level by STM and current imaging tunneling spectroscopy (CITS). This spectroscopy was applied to different types of square and star-like metal ion arrays, a supramolecular copper-oxygen assembly embedded into a polyoxotungstate wheel, and a coordination polymer based on amino acids, rendering local tunneling probabilities with submolecular resolution. These investigations allowed the localization of the positions of the incorporated transition metal centers due to a selective mapping of the coordinate metal-ligand bonds. CITS measurements of a one-dimensional, Fe containing polymer revealed a high contrast between the high-spin and the low-spin complexes.

CPP 1.6 Mon 11:15 H37

Balance of structure-building forces in aliphatic self-

assembled monolayers on metal substrates — ANDREY SHAPORENKO¹, TOBIAS WEIDNER¹, ANDREAS TERFORT², and •MICHAEL ZHARNIKOV¹ — ¹Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — ²Anorganische und Angewandte Chemie, Universität Hamburg, 20146 Hamburg, Germany

Using self-assembled monolayers (SAMs) of biphenyl-substituted alkaneselenols (BPnSe, where n = 2-6 is the number of the methylene units in the aliphatic linker) on gold and silver substrates as a model system, we demonstrate that the bonding configuration of the selenol headgroup is the deciding factor in the balance of structure-building interaction in the alkaneselenol SAMs. The energy associated with the persistence of this configuration is high enough to prevail over the energy gain associated with the optimal (i.e., dense) packing of the biphenyl moieties in the BPnSe SAMs. Considering, that the similar effects have been observed for the alkanethiolate SAMs, we can conclude on the generality of this phenomenon, stating that the exact bonding configuration of the headgroup is an important or, in most cases, even deciding factor in the balance of different contributions responsible for the molecular packing and structure of aliphatic self-assembled monolayers on metal substrates. This bonding configuration can be alternatively associated with a definite hybridization of the sulphur atom in the substrate-sulfur-carbon joint or a definite geometry of the adsorption site on the given substrate.

CPP 1.7 Mon 11:30 H37

Competitive Adsorption of Functionalized Molecules

on Semiconductor Nanocrystal Surfaces — KLEMENTYNA SZWAYKOWSKA^{1,2}, CHINNAPPAN RAJA^{3,4}, •THOMAS BLAUDECK^{1,3},

FRANK CICHOS^{1,5}, and CHRISTIAN VON BORCZYKOWSKI³ — ¹POM, TU Chemnitz, 09107 Chemnitz, Germany — ²Engineering and Applied Sciences, California Institute of Technology, Pasadena, CA 91125, USA — ³OSMP, TU Chemnitz, 09107 Chemnitz, Germany — ⁴ABMC, Kansas State University, Manhattan, KS 66506, USA — ⁵Molecular Nanophotonics, U Leipzig, 04103 Leipzig, Germany

Inorganic/organic aggregates from semiconductor nanocrystals and functionalized molecules such as porphyrins are considered building blocks in future nanoelectronics as they may provide control on the charge and energy transfer processes [1, 2]. We report on the formation process and the stability of aggregates comprising CdSe and CdSe/ZnS nanocrystals and TOPO ligands in toluene at ambient conditions. Applying steady-state spectroscopy to binary and ternary mixtures we compare the results in presence and absence of additional molecules. The experiments show that the formation kinetics is related to by the absolute concentration of the compounds in parallel to their molar ratio. The importance of the local TOPO concentration at the NC surface indicates a dynamic equilibrium governing the number of adsorption sites available. The findings are discussed in the light of Monte-Carlo simulations.

[1] E. Zenkevich et al., J. Phys. Chem. B 109, 8679 (2005).

[2] D. Kilin et al., J. Photochem. Photobiol. B (2006, in print).

CPP 1.8 Mon 11:45 H37

Grazing incident scattering for the investigation of crystallization in micellar systems — ●MAX WOLFF¹, ANDREAS MAGERL², and HARTMUT ZABEL¹ — ¹Lehrstuhl für Festkörperphysik/EP IV, Ruhr-Universität Bochum, 44780 Bochum, Germany — ²Lehrstuhl für Kristallographie und Strukturphysik, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Small angle scattering is known to provide information on the structural arrangement of block polymers. In highly dilute systems the conformation of the monomers is accessible from the radial intensity distribution. For higher concentrations micelles may appear and in the case of crystallisation usually an isotropic three dimensional powder is formed. From the resulting Debye-Scherrer rings it is difficult to determine the crystallographic structure. One way out is to introduce anisotropy by the application of shear. However, shear may affect the structure. Alternatively, by use of near surface small angle scattering, the ordering can be investigated close to the solid-liquid interface. We extracted detailed information on the crystallization of Pluronic (PEO-PPO-PEO) micelles solved in water in the vicinity of a solid substrate. We find the crystalline structure dependent on the chemical termination of the substrate as well as on the history of the sample. In addition we generally find large crystallites when entering into a crystalline phase from a liquid one that shrink in size further away from the phase boundary.

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CPP 1.9 Mon 12:00 H37

Self-assembly of diblock-copolymer micelles for template-based preparation of PbTiO₃ nanograins — STEPHAN KRONHOLZ¹, ●SILKE RATHGEBER², SILVIA KARTHÄUSER¹, HERMANN KOHLSTEDT¹, SVEN CLEMENS³, and THEODOR SCHNELLER³ — ¹Max-Planck Institute for Polymer Science, Polymer Physics, 55128 Mainz — ²Research Center Jülich GmbH, Center of Nanoelectronic Systems for Information Technology, 52425 Jülich — ³RWTH-Aachen, Institute of Materials for Electronic Engineering 2, 52074 Aachen

A bottom-up fabrication route for ferroelectric PbTiO₃ nanograins grown on predefined TiO₂ nanostructures used as seeds is presented.

[1] The structuring of the TiO₂ seeds is performed using a self-organized template constructed from a gold-loaded micellar monofilm. With this fabrication process, 12nm TiO₂ seeds and 30nm PbTiO₃ grains are prepared without any e-beam lithographic step. The dimensions of the structure imposed by the micellar template are transferred through all the processing steps to the final PbTiO₃ grains. By a combination of scattering experiments on the micellar solutions and a characterization of the monofilm we can determine whether the architecture of the diblock-copolymers in the micelles or the preparation conditions determine the quality and characteristics of the monofilm. It is shown that the intermicelle distance and the degree of order in the dried monofilm is mainly determined by the pulling velocity in the dipping process and the strength of the surface-micelle interaction, and not necessarily by the architecture of the diblock copolymers. [1] S. Kronholz et al., Adv. Funct. Mater. 16, 2346 (2006)

CPP 1.10 Mon 12:15 H37

Nanoaggregates on structured surfaces — ●HARALD GRAAF, THOMAS BAUMGÄRTEL, MAIK VIELUF, and CHRISTIAN VON BORCZYKOWSKI — Centre for nanostructured materials and analytics, TU Chemnitz, 09107 Chemnitz

Structuring of surfaces by local oxidation induced by electrical atomic force microscopy opens a way to prepare functional nanostructures. Different properties of the nanostructures compared to the surrounded surfaces can be adjusted by modifying the surface and nanostructure with various monolayers.

We report here on the selective binding of dye molecules as well as nanoparticles by non-covalent bonding. We used silicon (100) as substrates. The silicon surfaces were modified by a covalently bond alkene monolayer. The surface properties can be tuned by using functionalized alkene molecules. The monolayers are characterized by a high physical and chemical stability. By local anodic oxidation the monolayer can be locally degraded and the underlying silicon oxidized leading to silicon oxide nanostructure.[1] Dye molecules and nanoparticles were bond selectively to the nanostructure and/or the surrounding monolayer. Non-covalent interactions as ionic or hydrophobic interactions were responsible for this propose.[2]

[1] M. Ara, H. Graaf, H. Tada, Appl.Phys.Lett. 80(2002) 2565

[2] H. Graaf, M. Vieluf, C. von Borczykowski, submitted