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 Borczyskowski — 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 mm^2-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 Borczyskowski — 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 luminesence 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.

neselenols (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 selfassembled 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.

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