

## CPP 9: Nanoparticles II

Time: Monday 14:00–17:00

Location: ZEU 114

CPP 9.1 Mon 14:00 ZEU 114

**The influence of interfaces on fluorescence intermittency of single CdSe/ZnS nanocrystals** — ●CORNELIUS KRASSELT, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — TU Chemnitz, Institute of Physics, 09107 Chemnitz

Fluorescence intermittency, characterized by inverse power law distributions for both the bright and dark times, appears to be a common feature of many different classes of individual emitters [1].

Meanwhile it is generally accepted, that this behaviour is due to trapping and detrapping of charges. Two basic approaches, a tunneling model by Verberk [2] and the DCET model by Tang [3] try to explain the experimental circumstances associated with the blinking phenomena.

To contribute to the current discussion of the physical nature of blinking we investigated the influence of static trap sites in the local surroundings of ZnS overcoated CdSe nanocrystals spincoated on thermally grown silicon oxide. Therefore we have modified the trap density by annealing the silicon oxide substrate to reduce the amount of trapping silanol groups on the one hand and by passivation of the silicon oxide with an organic (ODS) monolayer on the other hand. Among the modification of the blinking statistics through the ODS-monolayer we found atypical distributions for the "on" time statistics which are different from a power law or exponential behaviour.

[1] F. Cichos et al.: COCIS 12 (2007), 272

[2] R. Verberk et al.: Phys. Rev. B 66 (2002), 233202

[3] J. Tang et al.: J. Chem. Phys. 123 (2005), 054704

CPP 9.2 Mon 14:15 ZEU 114

**Investigations to the Influences of Charges on the Fluorescence of Single CdSe/ZnS Quantum Dots Dependent on Crystal Size** — ●NICOLE AMECKE-MÖNNIGHOFF and FRANK CICHOS — Molecular Nanophotonics Group, Institute of Experimental Physics I, University Leipzig, Linnéstraße 5, 04103 Leipzig

The fluorescence properties of semiconductor nanocrystals (quantum dots) are intensively studied due to many potential applications, which want to make use of their tunable emission wavelength, high quantum yield and photon statistics. Considering their fluorescence in more detail many peculiarities can be found. Along those are antibunching, power-law blinking, lifetime-fluctuations and spectral diffusion. Most of those can be explained by charges close to or in the dot center leading to Auger processes (non-radiative energy transfer to those charges) and the quantum confined stark effect. Those charges can arise from ejection of electron or hole via tunneling leaving behind the counterpart and additionally changing the matrix charge constellation. We study all those characteristics on Qdot CdSe/ZnS crystals by time-resolved spectroscopy in particular as a function of crystal size. We find strong indications of fluctuating radiative and non-radiative rates for all sizes, however suggesting that the closer vicinity of the interface in smaller crystals is more stringent in switching the crystal either on or off.

CPP 9.3 Mon 14:30 ZEU 114

**The shape of CdSe nanoparticles and its role for their electro-optic properties in hybrid semiconductor-polymer structures** — ●FARZANA ASLAM<sup>1</sup> and CHRISTIAN VON FERBER<sup>2</sup> — <sup>1</sup>Department of Mathematics, Statistics and Engineering Sciences, Coventry University, Coventry, United Kingdom — <sup>2</sup>Applied Mathematics Research Centre, Coventry University, Coventry, United Kingdom

CdSe nanoparticles due to their electro-optical efficiency play an important role as sensitizers in hybrid semiconductor-polymer structures. Here, we study the electrostatic and structural trends of CdSe nanoparticles using empirical potentials. The electrostatic and structural properties of CdSe nanoparticles are studied as a function of the size, shape, structure and surface of the nanoparticles. We identify trends in the properties of particles that are either approximately spherical, cut along well defined crystal surfaces or short nano-rods. The aspect ratio of these particles has a significant impact on the energy, dipole moment and internal stress. We observe that the choice of the shape in terms of crystal surfaces and aspect ratio strongly affect the number of dangling bonds present on the surface of the nanocrystal, which in turn may determine the photo-generation and sensitization efficiencies. We study systematically both the mean behaviour of randomly

grown nanocrystals as well as the limiting cases of crystals with ideal crystal surfaces.

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**Study of electronic couplings between molecular and core states of 3-ethenylthiophene terminated Si quantum dots** — ●VINCENT GROENEWEGEN, VOLKER KUNTERMANN, CARLA CIMPEAN, ANJA SOMMER, and CAROLA KRYSCHI — Dept. Chemistry and Pharmacy, Physical Chemistry I and ICMM, FAU, Egerlandstr. 3, 91058 Erlangen

One of the central challenges in fabrication of silicon quantum dots (Si qdots) tailored for nano-optoelectronics is to functionalize their surfaces with electronically efficiently coupled molecules which mediate photogenerated carrier injection into the bulk and allow to optically control charge separation as well as luminescence properties of the bulk. We have developed a wet-chemistry procedure that allows to produce Si qdots with adjustable sizes and surface properties. Here we present a fs spectroscopy and a time-dependent density function theoretical (TDDFT) study of Si qdots with sizes around 2 nm which are terminated with 3-ethenylthiophene. The photoluminescence spectra as well as the TDDFT computations unambiguously show quasi-resonant electronic interactions between the excited states of covalently bound 3-ethenylthiophene and conduction band states of the Si core. These results were confirmed by ultrafast rise dynamics of absorption transitions of conduction band electrons which were monitored with the fs transient absorption spectroscopy technique

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**FRET and Non-FRET processes in quantum dot - dye nanoassemblies** — ●DANNY KOWERKO, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — Center of nanostructured materials and analytics, TU-Chemnitz, 09107 Chemnitz

Assemblies of semiconductor quantum dots (QDs - donor) and organic (dye - acceptor) molecules are of increasing interest for numerous applications in science and technology. Recent publications on such systems report on charge and fluorescence resonant energy transfer (FRET), prevalently neglecting an exact quantitative spectroscopic analysis of the acceptor. Recently, calculations of Seifert et al. [1] and Blaudeck and coworkers [2] demonstrated the crucial dependence of trap state emission from the surface coverage. In our contribution we emphasize the role of dye induced surface trap states as one mechanism - besides FRET - for QD quenching. Thus detailed quantitative analysis of titration experiments of differently functionalized perylenebismide molecules and CdSe/ZnS quantum dots will be discussed. By means of single particle spectroscopy we may even compare spectroscopic properties of the free and bound species on one and the same sample under identical conditions. Furthermore, analysis of FRET allows for a distinction between different geometries of the dye-QD assemblies.

[1] J. Frenzel, J.-O. Joswig, G. Seifert, J.Phys.Chem.C 2007, 111, 10761 [2] T. Blaudeck, E. I. Zenkevich, F. Cichos, C. von Borczykowski, J.Phys.Chem.C 2008, accepted

CPP 9.6 Mon 15:15 ZEU 114

**Optoelectronic properties of surface-modified Ge quantum dots** — ●IVAN LITZOV<sup>1</sup>, VINCENT GROENEWEGEN<sup>1</sup>, CAROLA KRYSCHI<sup>1</sup>, HARTMUT WIGGERS<sup>2</sup>, and DIETRICH HAARER<sup>3</sup> — <sup>1</sup>Dept. Chemistry and Pharmacy, Physical Chemistry I and ICMM, FAU, Egerlandstr. 3, 91058 Erlangen — <sup>2</sup>Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Lotharstr.1, 47048 Duisburg — <sup>3</sup>BIMF, University of Bayreuth, Universitaetsstr. 1, 95440 Bayreuth

This contribution is targeted to the development of functionalized Ge quantum dots tailored for optoelectronic applications such as solar cells and light emitting diodes. Ge qdots with sizes around 7 nm were successfully surface-modified via HF etching followed by thermal germylation with different unsaturated organic compounds. The surface modified Ge qdots exhibit photoluminescence peaking between 750 and 850 nm, while a fs spectroscopy study gave indication to photo-induced electron transfer from surface bound compounds to conduction band states of the Ge core. The eligibility of surface-modified Ge qdots for hybrid solar cells was studied by measuring photocurrent-action spectra and determining the power conversion efficiency for systematically varied compositions and thicknesses of P3HT:Ge qdot films

sandwiched by an ITO glass substrate and a LiF/Alu contact layer.

### 15 min. break

CPP 9.7 Mon 15:45 ZEU 114

**Enwrapping of tubular J-aggregates by Polyelectrolytes** — ●OMAR AL-KHATIB<sup>1,2</sup>, HELMUTH MÖHWALD<sup>1</sup>, JÜRGEN P RABE<sup>2</sup>, CHRISTOPH BÖTTCHER<sup>3</sup>, and STEFAN KIRSTEIN<sup>2</sup> — <sup>1</sup>Max-Planck-Institut of Colloids and Interfaces, Potsdam, Germany — <sup>2</sup>Humboldt University Berlin, Department of Physics, Germany — <sup>3</sup>Free University Berlin, Germany

Amphiphilic carbocyanine dyes are able to form tubular J-aggregates in aqueous solutions by a self-assembly process. The wall of the tubular aggregates is assumed to be formed by a dye bilayer that encloses the hydrophobic alkyl chains and exposes negative surface charges to the inside and outside of the aggregates. The charged surface is utilized to adsorb oppositely charged polyelectrolytes in order to enwrap the aggregate. This mechanism allows further stabilization and even functionalization using polyelectrolytes with functional groups. We show the coating of negatively charged tubular J-aggregates by various polycations such as poly(diallyldimethylammonium chloride) (PDAC), poly(allylamine hydrochloride) (PAH), and poly(ethylene imine) (PEI). The enwrapping was verified by cryogenic transmission electron microscopy (cryo-TEM) and its influence on the optical spectra was investigated. The morphology and the optical spectra of the coated structures vary considerably for the different polyelectrolytes and strongly depend on the ionic strength of the solution. The detailed investigation of these parameters allows to find controlled conditions for the formation of complex functionalized structures in aqueous solution by pure self assembling processes.

CPP 9.8 Mon 16:00 ZEU 114

**Polarization Resolved Emission of Single Nanotubular J-Aggregates** — ●DÖRTHE M. EISELE<sup>1</sup>, STEFAN KIRSTEIN<sup>1</sup>, JASPER KNOESTER<sup>2</sup>, JÜRGEN P. RABE<sup>1</sup>, and DAVID A. VANDEN BOUT<sup>3</sup> — <sup>1</sup>Humboldt University Berlin, Department of Physics, Germany — <sup>2</sup>University of Groningen, Institute for Theoretical Physics and Zernike Institute for Advanced Materials, Netherlands — <sup>3</sup>University of Texas at Austin, Department of Biochemistry and Chemistry, USA

Presently, the most efficient natural Light Harvesting System (LHS) contains multi-layer tubules of aggregated bacteriochlorophyll (BChl). Nanotubular J-aggregates of amphiphilic carbocyanine dyes constitute an artificial model system, which has been intensively studied in ensembles in solution. New insights into how the aggregate morphology affects its optical properties can be gained by directly probing individual single aggregates.

We deposited the aggregates onto solid transparent substrates by maintaining their optical and morphological properties. Single J-aggregates were identified using Atomic Force Microscopy (AFM). Near-field Scanning Optical Microscopy (SNOM) was used to simultaneously collect both topographic and fluorescent images of the single aggregates. The emission was recorded polarization resolved, and a quantitative analysis of the J-band emission polarization relative to the tube orientation was carried out. The emission is strongly but not perfectly polarized parallel to the long tubular axis, and the reduced linear emission dichroism of single tubes was determined to .

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**Spectroscopic study of the complex formation of DNA and a sequence specific minor-groove binding dye: towards molecular metallization** — ●MARKUS SCHUSTER<sup>1</sup>, GLENN BURLEY<sup>2</sup>, and ULRICH RANT<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>University of Leicester, UK

The complex formation of small molecules and DNA represents a promising concept to prepare self-assembled nanostructures. We investigate the interaction of DNA with 3,3\*-Diethylthiadicarbocyanine iodide (DiSC2(5)), which has been reported to selectively bind to the minor groove along ATATA sequences. Using extinction and fluorescence spectroscopy, we characterize the binding affinity of DiSC2(5) to different DNA sequences. Binding stoichiometries are determined using the method of continuous variation. The thermodynamic stability of the DNA/ DiSC2(5) complex is investigated and melting temperatures are analyzed. DiSC is found to associate with DNA as a dimer with increased, albeit not exclusive, affinity for the ATATA binding cassette.

Aiming to create metal nanoparticles on specific sites along DNA templates, we carried out metallization experiments using DiSC2(5)-dimers as site-selective seeds for metal growth. The development of silver nanoparticles is evidenced by the appearance of plasmon peaks in the absorption spectrum. Dynamic light scattering experiments reveal that the particle diameters range between 10 and 20 nm.

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**STM/CITS investigation of a Co(II) Cubane and a Zn(II) Coordination Polymer** — ●MICHAEL STOCKER<sup>1</sup>, UTPAL MITRA<sup>1</sup>, VIACHESLAV DREMOV<sup>1</sup>, NINA FISCHER<sup>2</sup>, FRANK W. HEINEMAN<sup>2</sup>, ANDREAS SCHEURER<sup>2</sup>, AYUK M. AKO<sup>2</sup>, NICOLAI BURZLAFF<sup>2</sup>, ROLF W. SAALFRANK<sup>2</sup>, and PAUL MÜLLER<sup>1</sup> — <sup>1</sup>Department für Physik, Universität Erlangen-Nürnberg, Germany — <sup>2</sup>Department für Chemie und Pharmazie, Universität Erlangen-Nürnberg, Germany

A combination of scanning tunneling microscopy (STM) and current imaging tunneling spectroscopy (CITS) has been performed on a Zn(II) coordination polymer ( $[Zn(L)(Cl)]_n$ ) and on a Co(II) cubane ( $[Co_4(HL)_4(Cl)_4]$ ). Both were deposited onto highly oriented pyrolytic graphite (HOPG). In the case of the Zn(II) coordination polymer thick strands as well as single polymer lines were observed. For the Co(II) cubane single molecules were observed. In CITS measurements we found a rather large contrast at the expected location of the Zn and Co metal centers, respectively. This demonstrates that the position of the metal centers within the molecule can be mapped. We discuss local tunneling spectroscopy data.

CPP 9.11 Mon 16:45 ZEU 114

**Solid State NMR for Polymer Nanocomposites** — ●ANASTASIA VYALIKH<sup>1</sup>, FRANCIS COSTA<sup>1,2</sup>, GERT HEINRICH<sup>1</sup>, DOMINIQUE MASSIOT<sup>3</sup>, and ULRICH SCHELER<sup>1</sup> — <sup>1</sup>Leibniz Institute of Polymer Research Dresden, Germany — <sup>2</sup>Borealis Polyolefine GmbH, Linz, Austria — <sup>3</sup>Université d'Orléans, France

Incorporating layered double hydroxide (LDH), which belongs to a class of synthetic clays with layered geometry, into polymers can significantly improve the materials properties even at low filler concentration. Compatibility with a non-polar polymer matrix and expansion of interlayer space in LDH are achieved by intercalation of surfactant molecules, that, in fact, can strongly affect the crystal structure of aluminium hydroxide layers.[1, 2] In the present work the 27Al MAS and 27Al triple-quantum (3Q)-MAS NMR has been applied in order to monitor stepwise the structural changes as a result of surfactant modification of LDH and to quantitatively characterise the resulting structures.[3] Additional insight is gained from high-resolution solid-state 1H NMR, which gives detailed information on protons in the layered structure, on water and the surfactant. [1] F.R. Costa, A. Leuteritz, U. Wagenknecht, D. Jehnichen, L. Häußler, and G. Heinrich, Appl. Clay Sci. 38 (2008) 153. [2] J. Rocha, M. del Arco, V. Rives, and Ulibarri, M.A., J. Mater. Chem. 9 (1999) 2499. [3] A. Vyalikh, D. Massiot, U. Scheler, Magn. Reson. Chem. (submitted)