

## CPP 7: Electronic and Optical Properties of Organic Systems II

Time: Monday 14:00–16:30

Location: H39

CPP 7.1 Mon 14:00 H39

**Controlling the optical properties of single molecules by optical confinement in a tunable microresonator** — ●ALEXEY CHIZHIK, RAPHAEL GUTBROD, ANNA CHIZHIK, SEBASTIAN BAER, and ALFRED MEIXNER — Institute of Physical and Theoretical Chemistry, University of Tuebingen, Auf der Morgenstelle 8, 72076 Tuebingen, Germany

We present experimental results on changing the fluorescence spectrum of a single dye molecule by embedding it within a tunable optical microresonator with subwavelength spacing. The resonator length is reversibly changed across the entire visible range with nanometer precision by using a piezoelectric actuator. By varying its length, the local mode structure of the electromagnetic field is changed together with the radiative coupling of the emitting molecule to the field. Since mode structure and coupling are both frequency dependent, this leads to a renormalization of the emission spectrum of the molecule. Moreover, we demonstrate how one can modify the ratio between the on- and off-axis photo emission of the molecules in the cavity. In addition, we use cylindrical vector laser beams (also known as doughnut laser modes) in the tunable microcavity to determine the longitudinal position of an isotropic emitter. By analyzing the excitation patterns resulting from the illumination of a single fluorescent bead in the focus of a radially polarized doughnut mode laser beam we can determine the longitudinal position of this bead in the microcavity with an accuracy of a few nanometers.

CPP 7.2 Mon 14:15 H39

**Time resolved 3D orientation spectroscopy - experimental realisation and simulation** — ●RICHARD BÖRNER<sup>1</sup>, DANNY KOWERKO<sup>2</sup>, CHRISTIAN VON BORCZYKOWSKI<sup>2</sup>, and CHRISTIAN G. HÜBNER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Lübeck, 23538 Lübeck, Germany — <sup>2</sup>Center for Nanostructured Materials and Analysis, Chemnitz University of Technology, 09107 Chemnitz, Germany

Confocal microscopy is a powerful tool for single molecule investigation of fluorescent macromolecules. Besides the common studied features in single molecule detection, the 3D orientation determination of the emission dipole enables the analysis of different conformational states. These conformational states can be represented as state depending dipole orientations intrinsic to the fluorescent molecule and/or in relation to the molecular frame. Furthermore, conformational states can be subject to intramolecular dynamics which may lead to spectral diffusion, fluorescence intensity and/or lifetime fluctuations and changes in the orientation of the emission dipole. Therefore, a simultaneous measurement of all parameters is mandatory. To this end, we show a detection scheme that allows for simultaneous determination of the full 3D emission dipole orientation, fluorescence intensity, the fluorescence lifetime and the emission spectra of single fluorescent molecules. We demonstrate the feasibility of our approach using pyridyl functionalized perylene bisimide (PBI). Moreover, monte-carlo simulations demonstrate the full potential of our detection scheme to quantify rotational dynamics on different time scales, in particular under confinement conditions.

CPP 7.3 Mon 14:30 H39

**Refined determination of anisotropic dielectric tensor of  $\alpha$ -PTCDA in the visible** — MARIA ISABEL ALONSO<sup>1</sup>, MIQUEL GARRIGA<sup>1</sup>, JOSEP ORIOL OSSO<sup>2</sup>, FRANK SCHREIBER<sup>3</sup>, LINUS GISSLEN<sup>4</sup>, and ●REINHARD SCHOLZ<sup>4</sup> — <sup>1</sup>Institut de Ciència de Materials de Barcelona, CSIC — <sup>2</sup>MATGAS, Campus de la Universitat Autònoma Barcelona — <sup>3</sup>Institut für Angewandte Physik, Universität Tübingen — <sup>4</sup>Walter Schottky Institut, Technische Universität München

Spectroscopic ellipsometry measurements obtained on the (102) surface of  $\alpha$ -PTCDA are analysed with an improved scheme for the propagation of the electromagnetic wave through the monoclinic crystal [1,2]. In this approach, the exact ellipsometric equations are solved numerically within a  $4 \times 4$  transfer matrix algorithm. The resulting dielectric tensor shows a pronounced anisotropy in the plane defined by the molecular transition dipoles oriented along the long axes of the two basis molecules in the unit cell, revealing a Davydov splitting of about 0.03 eV between the lowest subbands contributing to the optical response. The experimental findings are interpreted with

an exciton model accounting for Frenkel excitons and charge transfer states along the stacking direction, corroborating previous assignments of the charge transfer state below neutral molecular excitations [3].

- [1] M. I. Alonso, M. Garriga, N. Karl, J. O. Ossó, and F. Schreiber, *Org. Electron.* **3**, 23 (2002).  
 [2] M. I. Alonso and M. Garriga, *Thin Solid Films* **455-456**, 124 (2004).  
 [3] L. Gisslén and R. Scholz, *Phys. Rev. B* **80**, 115309 (2009).

CPP 7.4 Mon 14:45 H39

**Visualization of a Zn(II) coordination polymer and a trinuclear Cu(II) complex by STM/CITS** — ●U. MITRA<sup>1</sup>, M. STOCKER<sup>1</sup>, V. DREMOV<sup>1</sup>, N. FISCHER<sup>2</sup>, F. W. HEINEMANN<sup>2</sup>, A. ZHARKOUSKAYA<sup>3</sup>, N. BURZLAFF<sup>2</sup>, W. PLASS<sup>3</sup>, and P. MÜLLER<sup>1</sup> — <sup>1</sup>Department of Physics and Interdisciplinary Centre for Molecular Materials (ICMM), University of Erlangen-Nürnberg, Germany. — <sup>2</sup>Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Germany. — <sup>3</sup>Institut für Anorganische und Allgemeine Chemie, Universität Jena, Germany

Topographic measurements and current imaging tunneling spectroscopy (CITS) were performed on a Zn(II) coordination polymer  $[Zn(L)Cl]_n$  (L = deprotonated bis(N-methylimidazol-2-ylmethyl) acetic acid) and on a trinuclear Cu(II) complex based on triaminoguanidin ( $[Cu_3(bipy)_3(^H)TAG](ClO_4)$ ).  $10^{-9}$  molar solutions of the materials were deposited onto HOPG. In the case of the Zn(II) coordination polymer, strands of different thickness were observed. Molecular chains consisting of more than one molecule as well as clusters were also visualized for the trinuclear Cu(II) complex. In the CITS measurement, a very large current contrast was observed on the expected location of the Zn(II) and the Cu(II) metal centers. In this sense, we were able to map the internal coordination of the metal centers.

CPP 7.5 Mon 15:00 H39

**Excitation Energy Transfer in Pheophorbide-a Complexes: A Mixed Quantum Classical Computation** — ●JÖRG MEGOW, ZHENG-WANG QU, THOMAS RONNEBERG, BEATE RÖDER, and VOLKHARD MAY — Institut für Physik, Humboldt-Universität zu Berlin

The excitation energy transfer in a chromophore complex dissolved in ethanol is computed utilizing a mixed quantum classical methodology. The complex is formed by a butanediamine dendrimer to which four pheophorbide-a molecules are covalently linked. While all nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically utilizing a Frenkel-exciton model. A new approach is introduced to directly include intramolecular vibrations from MD-simulations into the former mixed quantum classical technique. Making a harmonic approximation to the single atom positions in respect of the so called reference structure atom positions a highly fluctuating energy was calculated and added to the chromophore complex Hamiltonian. This approach was used to further improve the existing calculations of excitation energy transfer, linear absorbance and time- and frequency resolved emission spectra, where the intramolecular vibrations were implemented parametrical only.

CPP 7.6 Mon 15:15 H39

**On the chain-length dependence of Förster energy transfer for conjugated oligomers** — ●RODRIGO QUEIROZ DE ALBUQUERQUE and ANNA KÖHLER — University of Bayreuth, Physics Department, Universitätsstr. 30, 95440 Bayreuth, Germany.

Energy transfer systems comprising donor-acceptor molecules have been successfully described using the Förster theory, which uses the Point-Dipole Approximation, PDA. However, for organic semiconductors containing extended chromophores rather small donor-acceptor distances are frequently found, and the PDA is well known to fail in correctly describing the energy transfer process. Here we report a combined experimental and theoretical study of energy transfer systems containing oligofluorenes with different conjugated chain lengths as donors and an anthracene derivative as acceptor. Blends with different amounts of donor and acceptor are investigated by means of steady-state and time-resolved spectroscopy, and the PDA is used to calculate energy transfer parameters. Our aim is also to examine the

validity of the PDA in the present case, as well as to discuss the influence of the conjugated chain length of the oligofluorenes on the photophysics of the donor-acceptor systems described here.

CPP 7.7 Mon 15:30 H39

**Visualizing the spin states of surface deposited Fe(II) spin-crossover compounds** — •M. STOCKER<sup>1</sup>, M. S. ALAM<sup>1</sup>, A. VOLKOV<sup>1</sup>, U. MITRA<sup>1</sup>, K. GIEB<sup>1</sup>, M. HARYONO<sup>2</sup>, K. STUDENT<sup>2</sup>, A. GROHMANN<sup>2</sup>, V. DREMOV<sup>1</sup>, and P. MÜLLER<sup>1</sup> — <sup>1</sup>Department of Physics and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Germany. — <sup>2</sup>Institut für Chemie, Technische Universität Berlin, Germany.

We present a novel method for determining the spin states of individual molecules and small clusters of surface deposited Fe(II) spin crossover (SCO) compounds by STM. Here we focus on  $[\text{Fe}^{II}(\text{L})_2(\text{BF}_4)_2]$  ( $\text{L}=2,6\text{-di}(1\text{H-pyrazol-1-yl})\text{-4-(thiocyanatomethyl)pyridine}$ )<sup>1</sup>. For comparison, a high spin (HS) compound with a similar coordination motif was investigated.  $10^{-8}$  molar solutions of the materials were drop-coated onto HOPG substrates and investigated by STM and CITS. A strong contrast between two distinct states of the SCO compound was found in the conductivity map, whereas the HS reference molecules always showed the same contrast. Therefore, the two different states can be identified with the high spin and low spin states. Switching of the spin state from high- to low-spin state and vice versa were observed at room temperature. Indications for a widening of the spin transition were found by varying the temperature.<sup>2</sup>

<sup>1</sup> M. Haryono, et al., Eur. J. Inorg. Chem. 2009, 2136.

<sup>2</sup> M.S. Alam, et al., Angew. Chem. (2009) (accepted).

CPP 7.8 Mon 15:45 H39

**Conjugated Polymers and Fullerenes Under Oxygen Exposure: An Electron Spin Resonance Study** — •HANNES KRAUS<sup>1</sup>, ANDREAS SPERLICH<sup>1</sup>, CARSTEN DEIBEL<sup>1</sup>, and VLADIMIR DYAKONOV<sup>1,2</sup> — <sup>1</sup>Experimental Physics VI, Physical Institute, Julius-Maximilians-University of Würzburg, D-97074 Würzburg — <sup>2</sup>ZAE Bayern, Div. Functional Materials for Energy Technology, D-97074 Würzburg

For applications in polymer bulk heterojunction solar cells, the blend of the polythiophene P3HT and the fullerene electron acceptor material PCBM is one of the most promising model systems until now. On the way to industrial scale processing of solar cells from these materials, the stability issue and thus the understanding of degradation mechanisms due to environmental conditions is crucial. We study the light-induced creation of polymer:oxygen-charge transfer complexes in air-exposed P3HT with electron spin resonance, and simultaneously record the evolution of the photoluminescence quenching. We identify two separate photochemical processes leading to these results, and corroborate our findings with triplet-sensitive optically detected mag-

netic resonance (ODMR) measurements. Furthermore, we propose a protective effect of PCBM on P3HT through triplet quenching in organic solar cells.

CPP 7.9 Mon 16:00 H39

**PDMS-enclosed Liquid Crystal Lasers for Lab-On-Chip Applications** — •JÜRGEN SCHMIDTKE and EUGENE M. TERENTJEV — Cavendish Laboratory, University of Cambridge, UK

During the past decade, self-assembled photonic band edge lasers based on cholesteric liquid crystals have attracted considerable interest as microscopic, coherent light sources. We demonstrate the operation of such a laser confined between optically clear and elastic polydimethylsiloxane (PDMS) rubber substrates. The formation of a planar helical texture in the cholesteric film was supported by microstructuring of PDMS layer surface, using the nano-embossing technique with glass substrates coated with conventional alignment layers as a template. With PDMS being the standard material for the fabrication of microfluidic devices, this opens a simple and flexible route for the integration of microscopic laser sources for lab-on-chip applications like spectroscopy, photo-chemistry or fluorescence cytometry.

CPP 7.10 Mon 16:15 H39

**The Spectral diffusion in poly(para-phenylene)-type polymers with different energetic disorder** — •SEBASTIAN T. HOFFMANN<sup>1</sup>, HEINZ BÄSSLER<sup>2</sup>, JAN-MORITZ KOENEN<sup>3</sup>, MICHAEL FORSTER<sup>3</sup>, ULLRICH SCHERF<sup>3</sup>, ESTER SCHELER<sup>4</sup>, PETER STROHRIEGL<sup>4</sup>, and ANNA KÖHLER<sup>1</sup> — <sup>1</sup>Dept. of Physics, Univ. of Bayreuth — <sup>2</sup>Physical Chemistry, Philipps-Univ. Marburg — <sup>3</sup>Macromol. Chemistry, Bergische Univ. Wuppertal — <sup>4</sup>Dept. of Chemistry, Univ. of Bayreuth

We have employed quasi continuous fluorescence and phosphorescence spectroscopy within a temperature range between 10K and 500K to monitor the spectral diffusion of singlet and triplet excitons in a series of pi-conjugated polymers. We investigated (i) how spectral diffusion is controlled by the degree of energetic disorder present in the amorphous film, and (ii) how this process depends on the range of the electronic coupling. For singlets, and for triplets in low-disorder compounds, spectral diffusion results in a bathochromic shift of the fluorescence spectra upon cooling, until saturation sets in. In contrast, for triplets in systems with at least moderate disorder, spectral diffusion is kinetically frustrated, i.e. frozen-out.[1] This is evident through a hypsochromic shift of the phosphorescence spectra upon cooling below a characteristic temperature. The frustration effect is controlled by the jump distance, and thus it is specific for triplet excitations that migrate via short range coupling among strongly localized states as compared to singlet excitons.

[1] S.T. Hoffmann et al, Phys. Rev. B, submitted.