

## CPP 22: POSTER: INTERNAL SYMPOSIUM Optical Spectroscopy

Time: Wednesday 16:00–18:30

Location: Poster B

CPP 22.1 Wed 16:00 Poster B

**FTIR and EPR Studies of the Adsorption Complexes of Benzene and Oxygen on Cu/HZSM5 Zeolites** — ●AUGUSTA ÈNE, TANJA ARCHIPOV, and EMIL RODUNER — Institute of Physical Chemistry, University of Stuttgart

Today phenol is produced mostly by the Cumene process, a three-step process which yields phenol and acetone in an 1:1 ratio. An alternative to this synthesis is the oxidation of benzene to phenol with molecular oxygen on Cu-exchanged zeolite catalysts. In order to understand the catalytic process on a molecular level one needs to understand the structures and geometry of the reactants on the surface. Vibrational spectroscopy offers information on both the strength of the acid sites and the nature of the adsorbate. Thus we study the adsorption complexes of benzene and oxygen on Cu-containing and Cu-free HZSM-5 zeolite by means of FTIR spectroscopy in order to determine the orientation of the adsorbed molecules on the zeolite surface. As the  $Cu^{2+}$  ions (3/2 spin) are EPR active, the oxidations state of Cu can be observed as well. Information on the surroundings of the active Cu species can be gained from the g and hyperfine anisotropy, offering us the chance to determine which Cu containing sites are more active during the catalytic process.

CPP 22.2 Wed 16:00 Poster B

**Revealing the Electron-Phonon Coupling in a Conjugated Polymer by Single-Molecule Spectroscopy** — ●RICHARD HILDNER<sup>1</sup>, ULRICH LEMMER<sup>2</sup>, ULLRICH SCHERF<sup>3</sup>, MARIN VAN HEEL<sup>4</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimentalphysik IV, Universität Bayreuth, 95440 Bayreuth, Germany — <sup>2</sup>Lichttechnisches Institut, Universität Karlsruhe (TH), 76131 Karlsruhe, Germany — <sup>3</sup>Fachbereich C, Universität Wuppertal, 42097 Wuppertal, Germany — <sup>4</sup>Department of Biological Sciences, Imperial College London, London SW7 2AY, United Kingdom

The efficiency of charge- and energy-transfer processes in  $\pi$ -conjugated polymers is strongly determined by their electron-phonon coupling strength. However, the inherent pronounced structural disorder as well as the strong spectral diffusion in this class of functional materials prevented a direct determination of this parameter as yet. Here we employ single-molecule spectroscopy in combination with pattern recognition techniques which allows us to retrieve the profile of the electronic spectrum and concomitantly the electron-phonon coupling strength in a methyl-substituted ladder-type poly(*para*-phenylene) (MeLPPP). From these data we find a weak electron-phonon coupling for this polymer at low temperatures consistent with the fast excitation energy transfer processes that have been observed for this polymer. Moreover, we find strong evidence that the low-frequency vibrational modes, which are coupled to the electronic transitions, stem from vibrations of the surrounding host matrix indicating an even weaker intra-chain electron-phonon coupling in MeLPPP.

CPP 22.3 Wed 16:00 Poster B

**Fluorescence Lifetime Imaging Microscopy (FLIM) in the Frequency Domain** — WILHELM HÜTTNER and ●LOTHAR KADOR — Universität Bayreuth, Physikalisches Institut und Bayreuther Institut für Makromolekülforschung (BIMF), 95440 Bayreuth

We report the design and construction of a confocal fluorescence lifetime imaging microscope (FLIM) based on a cw laser which is amplitude-modulated in the MHz range. Fluorescence lifetimes are calculated from the phase shift between the fluorescence signal and the excitation. The concept is inspired by a recent publication by Booth and Wilson [1] and allows one to choose different modulation frequencies between about 28 and 50 MHz. First experimental data are presented for blotting paper stained with a laser dye.

[1] M. J. Booth and T. Wilson, *J. Microsc.* **214**, 36 (2004).

CPP 22.4 Wed 16:00 Poster B

**Mapping the Diffusional Landscape of a Porous Nanostructure** — ●JOHANNA KIRSTEIN, ANDREAS ZÜRNER, STEFFEN SCHMIDT, MARKUS DÖBLINGER, THOMAS BEIN, and CHRISTOPH BRÄUCHLE — Dept. Chemie und CeNS, LMU München, Germany

Single Molecule Spectroscopy (SMS) is used in combination with Transmission Electron Microscopy (TEM) to trace out the internal structure of mesoporous thin films and to gain insight into the diffu-

sion dynamics with respect to the underlying structure of the host. Individual dye molecules acting as molecular beacons are incorporated into the pores and their diffusion pathway through the pore system is observed by optical widefield microscopy. However, structural features on the nanometer scale can not be observed by optical methods. To resolve the pore structure in detail TEM measurements are needed. Usually, the sample preparation for TEM is either time-consuming, when it involves the preparation of cross-sections, or it lifts the film off its substrate by scratching. With such methods it is thus not possible to directly correlate the nanopore structure of the film and the trajectories of the dye molecules obtained by SMS.

Here, we present the synthesis of thin mesoporous films loaded with fluorescent dye molecules that can be successively investigated by optical widefield microscopy and TEM. We developed a method to overlay the images obtained by the two methods. This is the first time that dynamical information from single particle diffusion can be directly correlated with the structural details of the porous host obtained by TEM.

CPP 22.5 Wed 16:00 Poster B

**Tunneling Events in Methyl-Substituted Terrylene in a Hexadecane Matrix** — ●ALFRED SIGL<sup>1</sup>, ANDRE GOURDON<sup>2</sup>, MICHEL ORRIT<sup>3</sup>, and JOSEF FRIEDRICH<sup>1</sup> — <sup>1</sup>TUM, München, Germany — <sup>2</sup>CEMES, Toulouse, France — <sup>3</sup>MoNOS, Leiden, Netherlands

We investigated methyl-substituted terrylenes in a crystalline hexadecane matrix via hole-burning and single-molecule spectroscopy with the goal to detect single rotational tunneling events of the methyl group. A methyl group is a perfect tunneling system since there is no energy asymmetry. The rotational tunneling states correlate strictly with the nuclear spin states of the hydrogens. The hole burning experiments show a very unusual pattern: symmetric to the central hole appear two extremely sharp (200 MHz broad) antiholes, two broader antiholes and two sideholes. We associate the sharp antiholes, shifted by 1.3 GHz from the central hole, with the rotational tunneling states of the terrylene methyl group and the remaining features (5.1 and 6.4 GHz from the central hole) with a structural Two Level System involving the hexadecane lattice. The jumps in the frequency trajectories of single  $\beta$ -terrylene molecules reflect the 5.1 and 6.4 GHz features found in the hole-burning experiments. However, light-induced frequency jumps of single molecules corresponding with the 1.3 GHz features could not be detected. A possible reason could be that the high intensities in the single-molecule experiment pump the tunneling system to one of its substates.

CPP 22.6 Wed 16:00 Poster B

**Incorporation of in vitro Synthesized GPCRs into Peptide Tethered Artificial Membrane Sensor Platforms** — ●RUDOLF ROBELEK<sup>1</sup>, MARCEL LEUTENEGGER<sup>2</sup>, THEO LASSER<sup>2</sup>, WOLFGANG KNOLL<sup>1</sup>, and EVA-KATHRIN SINNER<sup>1</sup> — <sup>1</sup>Max-Planck-Institute for Polymer Research; Ackermannweg 10; 55128 Mainz; Germany — <sup>2</sup>Laboratoire d'optique biomédicale; EPFL; Lausanne; Switzerland

In the last decade the optical spectroscopy techniques and biosensors have made a tremendous progress. Against this background it strikes that the study of complex membrane proteins, including the pharmacologically very important class of G protein coupled receptors, is rarely covered by this development. The main reason therefor is the difficult accessibility and availability of these proteins in biosensoric systems that are adapted for optical spectroscopic techniques. To overcome the named problems we here present a new concept using an in vitro expression strategy to directly insert complex membrane proteins into peptide tethered lipid bilayers. The result of this approach, which is demonstrated for the odorant receptor OR5, is a vectorial insertion of the protein under full conservation of its biological function. The protein / biosensor system can then be characterized in detail by different kinds of optical spectroscopic techniques. In our case we applied SPFS, SEIRAS and TIRF-Imaging to characterize the odorant receptor OR5 in a peptide tBLM. The successful transfer of this concept to further protein examples indicates, that the presented strategy could be a versatile platform to make the broad field of complex membrane proteins available to a multitude of optical spectroscopic techniques.

CPP 22.7 Wed 16:00 Poster B

**Optical properties of rubrene crystals and films as a function of temperature** — OLGA KRYLOVA<sup>1</sup>, DOMINK BERG<sup>1</sup>, ●MATTHIAS MÜLLER<sup>1</sup>, JENS PFLAUM<sup>2</sup>, and MORITZ SOKOLOWSKI<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Bonn, — <sup>2</sup>3. Physikalisches Institut, Universität Stuttgart

We have investigated the optical absorption and photoluminescence (PL) of high quality rubrene (Rub) single crystals and thin vacuum deposited Rub films as a function of temperature. Interestingly, very strong changes are found in the PL spectra of Rub crystals upon cooling. Whereas room temperature (RT) spectra show the strongest emission at about 2000 cm<sup>-1</sup> below the electronic origin, spectra at low temperatures (LT), i.e., 5 K, have a very strong emission on the electronic origin and are very similar to spectra of thin Rub films. Going to low T increases the PL yield by a factor of more than 100. These results are tentatively interpreted with an emission from H-aggregates at RT and from J-aggregates at LT. A detailed comparison with the spectra of Rub films and Rub in solution will be given. Funding by the DFG research unit 557 is acknowledged.

CPP 22.8 Wed 16:00 Poster B

**Diffusion of biomolecules in mesoporous silica materials** — ●TIMO LEBOLD, CHRISTOPHE JUNG, JOHANNA KIRSTEIN, LEA MÜHLSTEIN, THOMAS BEIN, and CHRISTOPH BRÄUCHLE — Center for Nanoscience, Ludwig-Maximilians-Universität München, Department Chemie und Biochemie, Butenandtstraße 5-13, Haus E, 81377 München, Germany

Nanoporous channel systems, for example M41S-materials, form a class of very promising host systems. Various guests can be embedded into their pores. A highly interesting application could be drug-delivery systems based upon such mesoporous silica materials. However, an essential prerequisite for the development of such systems is the detailed knowledge of the molecular dynamics and the host-guest interactions within the porous network. The diffusional behaviour of fluorescent molecules is elucidated in our group by highly-sensitive single-molecule microscopy techniques: wide-field and confocal fluorescence microscopy. They provide a unique insight into the molecular trajectories and the underlying mechanisms. This study focuses on fluorescently labelled biomolecules which are incorporated as guests into calcined mesoporous structures as well as structures with an internal functionalization of the pores. Their dynamics and their interaction with the pore inner surface are investigated in detail. This allows us to characterize the diffusion processes that are essential for the release of biomolecules from mesoporous silica materials in their role as drug-delivery systems.

CPP 22.9 Wed 16:00 Poster B

**Femtosecond Resolved Transient Absorption Spectroscopy of Silicon Quantum Dots** — ●VOLKER KUNTERMANN<sup>1,2</sup>, CARLA CIMPEAN<sup>1</sup>, DIETRICH HAARER<sup>2</sup>, and CAROLA KRYSCHI<sup>1</sup> — <sup>1</sup>Department for Physical Chemistry I, Friedrich-Alexander-Universität — <sup>2</sup>Experimentalphysik/BIMF, Universität Bayreuth

We report about femtosecond resolved transient absorption spectroscopy of quantum dot semiconductor nanoparticles. The silicon nanoparticles with a diameter of 5 nm were synthesized by a gas phase process. The diameter is in the order of the exciton radius. The time resolved experiments are always in the limit of strong confinement. Performing stationary fluorescence spectroscopy we find two characteristic bands, which arise on the one hand from bulk excitons of the nanoparticles and on the other hand from surface states in the outer shell. The basis for all possible applications, e.g. photovoltaics, is a well defined and stable surface. With time resolved spectroscopic investigations we get insight in the surface quality and in the passivation of the quantum dots since the observed surface luminescence is highly sensitive to physisorbed compounds (e.g. different functionalisations).

CPP 22.10 Wed 16:00 Poster B

**Photothermal Microscopy of Single Gold Nanoparticles in Polymers** — ●ROMY RADÜNZ and FRANK CICHOS — Molecular Nanophotonics, Universität Leipzig, Linnéstraße 5, 04103 Leipzig

Photothermal microscopy is an optical imaging technique, which is based on the release of heat of an absorbing nanoobject to its local surrounding. The temperature rise in the surrounding induces a local refractive index change, which can be detected optically. Thus non-fluorescent nanoobjects such as gold particles of only a few nanometer in size become visible. It is generally expected that the photothermal signal scales with the volume of the nanoobject due to the depen-

dence of the absorption cross-section on the volume. We show that this relation does not hold due to the influence of the nanoparticle surface on the heat transfer from the gold particle to the environment. Numerical calculations and experimental results demonstrate that the dependence of the photothermal signal on the particle size is weaker than expected due to the surface conductivity of the nanoparticle. As a consequence, this type of experiments provides new routes to explore local thermal properties as well as the physics of heat conduction on the nanoscale.

CPP 22.11 Wed 16:00 Poster B

**Vibrational Sum Frequency Scattering on Biomedical Poly (lactic acid) Microspheres** — ●ALBERT SUGIHARTO<sup>1</sup>, CLAES MAGNUS JOHNSON<sup>1</sup>, MARC SMITS<sup>2</sup>, JOHANNES NIJSEN<sup>3</sup>, and SYLVIE ROKE<sup>1</sup> — <sup>1</sup>MPI for Metals Research, Stuttgart, Germany — <sup>2</sup>FOM-Institute AMOLF, Amsterdam, The Netherlands — <sup>3</sup>Departement of Nuclear Medicine, University Hospital, Utrecht, The Netherlands

Biodegradable poly(lactic acid)(PLA) microspheres have recently been applied as a medicine against liver cancer [1]. In this proposed treatment, one injects polymer particles loaded with radioactivated heavy metal (Ho) complex into hepatic artery. The particles are transported to the tumor site, and from there irradiate and destroy the tumor cells. To understand the interaction of these particles with the body, it is important to investigate the bulk and surface structure of these particles on a detailed molecular level.

We have probed the particle structure using vibrational sum frequency scattering [2], a novel technique that combines all the advantages of vibrational sum frequency generation (SFG) with light scattering. This means one can obtain information about both the bulk and the surface structure on the molecular level as well as particle shape and size. We find that the PLA microspheres consist of crystallite domains, in which two adjacent helical PLA chains are arranged anti-parallel to each other. Furthermore we observed crucial structural changes between microspheres with and without medicinal complex.

[1] J.F.W. Nijsen et al., Eur. J. Nucl. Med. 26, 699 (1999)

[2] S. Roke et al., Phys. Rev. Lett. 91, 258302 (2003)

CPP 22.12 Wed 16:00 Poster B

**Characterization of novel acceptor materials for photovoltaic application by optical spectroscopy methods** — ●MORITZ LIEDTKE<sup>1,2</sup>, ANDREAS WÖRLE<sup>1</sup>, JOHANNES SIEGER<sup>1</sup>, CARSTEN DEIBEL<sup>1</sup>, VLADIMIR DYAKONOV<sup>1,2</sup>, INGO RIEDEL<sup>2</sup>, and NAZARIO MARTIN<sup>3</sup> — <sup>1</sup>Experimental Physics VI, Physical Institute, Julius-Maximilians University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — <sup>2</sup>Div. Functional Materials for Energy Technology, ZAE Bayern e.V., Am Hubland, D-97074 Würzburg, Germany — <sup>3</sup>Departamento de Química Organica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain

Polymer-Fullerene composites are used in photovoltaic applications due to their efficient charge carrier generation. One approach to improve power efficiencies of bulk heterojunction solar cells are new material combinations in which the low absorbing C60 derivative (PCBM) is replaced by an optically active C70 based methanofullerene. We compared blends of poly(3-hexylthiophene) (P3HT) and [6,6] phenyl-C61-butyric acid methyl ester to blends of two C70 based fullerene molecules mixed with P3HT. We studied the formation of excited states, their lifetimes and charge transfer reactions with respect to blend ratio and temperature by optical spectroscopy techniques such as photoinduced absorption (PIA) and frequency dependent PIA measurements.

CPP 22.13 Wed 16:00 Poster B

**Photophysics of functionalized perylenbisimides as building blocks for dye - quantum dot nanoassemblies** — ●DANIELA TÄUBER, DANNY KOWERKO, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — Center of nanostructured materials and analytics, TU-Chemnitz, 09107 Chemnitz

Organic - inorganic building blocks promise numerous applications in nanoelectronics, biology and physics. Organic dye molecules in combination with semiconductor quantum dots are good candidates to study chemistry and physics of organic-inorganic interfaces at molecular level. However, characterization of such complexes first requires careful analysis of the elementary building blocks. Thus we report here on polarization resolved single molecule spectroscopy as a powerful tool for characterizing the different rotational and conformational dynamics of functionalized perylenebisimides. Such functionalized dyes with different anchor groups are used by us in prototype dye quantum dot

nanoassemblies. Perylenebisimide dyes are known to show rich dynamics, including intramolecular flips which will result in intensity fluctuations. Polarization resolved detection allows for a discrimination of those intramolecular flips against rotations of the complete molecule.

CPP 22.14 Wed 16:00 Poster B

**Single-laser-pulse-induced switching of molecular spin states**

— ●SÉBASTIEN BONHOMMEAU<sup>1</sup>, NIKO PONTIUS<sup>1</sup>, HERMANN DÜRR<sup>1</sup>, WOLFGANG EBERHARDT<sup>1</sup>, SAIOA COBO<sup>2</sup>, GABOR MOLNÁR<sup>2</sup>, and AZZEDINE BOUSSEKSOÛ<sup>2</sup> — <sup>1</sup>Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H (BESSY), Albert-Einstein-Straße 15, 12489 Berlin, Germany — <sup>2</sup>Laboratoire de Chimie de Coordination, CNRS UPR-8241, Route de Narbonne 205, 31077 Toulouse, France

Light-induced phenomena in spin crossover complexes have aroused a lot of interest since the discovery of the LIESST (Light-Induced Excited Spin State Trapping) effect in solid state. Here, we demonstrate by means of Raman spectroscopy that a bi-directional spin transition can be obtained at room temperature when applying a nanosecond laser pulse in the hysteresis loop of the spin crossover complex Fe(pyrazine)[Pt(CN)<sub>4</sub>]. This phenomenon is interpreted as a photo-induced phase transition exhibiting a threshold energy density. In order to provide a deeper insight on the electronic properties of such polymeric materials, X-ray photoemission and absorption experiments have also been performed on a multilayer assembly of thin films of Fe(azopyridine)[Pt(CN)<sub>4</sub>] that display spin crossover. This information is of paramount importance to shed new light on the photo-induced dynamics, in the subpicosecond time scale, which will be investigated using the femtoslicing facility now available at BESSY GmbH.

CPP 22.15 Wed 16:00 Poster B

**Spectra of molecular aggregates and energy transfer dynamics: a novel approach**

— ●LARS ERIK WÜRFLINGER, WOLFGANG WOLFF, and WALTER STRUNZ — Physikalisches Institut, Universität

Freiburg, Hermann-Herder-Straße 3, D-79104 Freiburg

Although dye polymer aggregates have been studied since the mid-thirties (J-band), in the last few years there has been a feverish re-awakening of interest in this area [1, 2]. Based on a recently developed stochastic Schrödinger equation [3], we study exciton transfer dynamics fully including the influence of intramolecular vibrations of arbitrary spectral density. The efficiency of our approach allows us to calculate absorption spectra of aggregates composed of an arbitrary number of monomers. Furthermore we are able to describe the full range from coherent to incoherent transfer in a unified way.

[1] V. May, O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH)

[2] A. Eisfeld, J. S. Briggs, *Chem. Phys.* **281**, 61, *Chem. Phys.* **324**, 376

[3] T. Yu, L. Diósi, N. Gisin, W.T. Strunz, *Phys. Rev. A* **60**, 91

CPP 22.16 Wed 16:00 Poster B

**Monitoring of Single-Chromophor Lifetime Fluctuations by Single-Photon Autocorrelation**

— RUBEN SCHMIDT<sup>1</sup>, ●THOMAS BLAUDECK<sup>1</sup>, ACHIM GRUBER<sup>1,2</sup>, and FRANK CICHOS<sup>1,2</sup> — <sup>1</sup>Photonics and Optical Materials, TU Chemnitz, 09107 Chemnitz, Germany — <sup>2</sup>Molecular Nanophotonics, 04103 Leipzig, Germany

We report on a technique of time-resolved single-photon counting to monitor the fluctuations in the fluorescence lifetime of single chromophors. When analyzing the single-photon data in terms of a lifetime-intensity correlation, fluctuations can be assigned to either the radiative or the non-radiative decay rate of the excited state. In particular, the case of highly non-exponential fluorescence decays observed for semiconductor nanocrystals is discussed. Here, single-photon autocorrelation allows to assign a change of the fluorescence lifetime on the timescale of several microseconds. This reveals the emissive state to be rather a distribution of states than a single one.