# DS 34: Organic thin films II: Interface spectroscopy

Time: Thursday 15:00–17:30 Location: H 2032

DS 34.1 Thu 15:00 H 2032

**Nature of interactions at interfaces between transition metal phthalocyanines and metals** — •Heiko Peisert, Fotini Petraki, Umut Aygül, Florian Latteyer, Johannes Uihlein, and Thomas Chassé — University of Tuebingen, Institute of Physical Chemistry, Auf der Morgenstelle 18, 72076 Tuebingen, Germany

Transition metal Pcs (TMPcs) are potential candidates for various applications, most recently they are considered as a promising material for the development of low dimensional molecular magnets or organic spintronic devices. Although electronic properties of TMPcs have been extensively investigated, results are controversial discussed. Moreover, the nature of the interaction at several interfaces is still unclear. In particular, the involvement of the central metal atoms seems to be a key issue for the electronic interface properties. The contribution gives an overview about our recent studies on the interaction of TMPcs (TM: Mn [1], Fe, Co [2,3], Ni) at metal interfaces (Au, Ag) using mainly photoexcited electron spectroscopies (photoemission, resonant photoemission, X-ray absorption). In all cases, charge transfer processes from metallic substrates to the metal 3d levels of the phthalocyanine molecule occur. However, the detailed electronic situation depends clearly on the system under consideration.

[1] F. Petraki, H. Peisert et al., J. Phys. Chem. C 115 (2011) 21334.

[2] H. Peisert, I. Biswas, U. Aygül, A. Vollmer, T. Chassé, Chem. Phys. Lett. 493 (2010) 126.

[3] F. Petraki, H. Peisert et al., J. Phys. Chem. Lett. 1 (2010) 3380.

DS 34.2 Thu 15:15 H 2032

**Origin of pinning-levels at molecularly modified electrodes** — •Stefanie Winkler[1], Ralf-Peter Blum[2], Ralph Rieger[3], Joachim Räder[3], Jürgen P. Rabe[2], Klaus Müllen[3], and Norbert Koch[1,2] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str.15. 12489 Berlin — [2]Humboldt-Universität zu Berlin, Institut für Physik, 12489 Berlin — [3]Max Planck Institute für Polymerforschung, Ackermannweg 10, 55128 Mainz

Our photoemission study reveals pronounced work function ($\phi$) increases by up to 2.0 eV when a strong electron acceptor monolayer comprising tetrafluoro-tetracyanoquinodimethane or hexaazatriphenylene-hexacarbonitrile is deposited on indium tin oxide (ITO) surfaces (pristine ITO $\phi$: 4.2 eV). This increase is attributed to a charge-transfer type interaction between ITO and the acceptors, involving partial filling of the LUMO of pristine acceptors. The evolution of sample $\phi$ and hole injection barrier upon incremental deposition of the hole transport material N,N'-bis(1-naphthyl)-N,N'-diphenyl- 1,1'-biphenyl-4,4'-diamine ($\alpha$-NPD) is reported, for both type of acceptor modified ITO electrodes. We find that the onset of the highest molecular level of multilayer $\alpha$-NPD is pinned 0.5 eV below the Fermi-level. Surprisingly, pinning is achieved at about 0.4 eV higher initial electrode $\phi$ (5.2 eV) than would be expected according to the ionization energy of $\alpha$-NPD (5.3 eV). $\phi$ inhomogeneities at sub-monolayer acceptor coverages, resulting in laterally adjacent pinned and unpinned $\alpha$-NPD on top, can explain this unexpected behaviour, which highlights the importance of knowing sample inhomogeneities on the molecular scale.

DS 34.3 Thu 15:30 H 2032

**Tuning the work function of ZnO with a molecular electron acceptor** — •Raphael Schlesinger[1], Yong Xu[3], Stefanie Winkler[2], Antje Vollmer[2], Patrick Rinke[3], Matthias Scheffler[3], Sylke Blumstengel[1], Fritz Henneberger[1], and Norbert Koch[1,2] — [1]Humboldt-Universität zu Berlin — [2]Helmholtz-zentrum Berlin, BESSY II — [3]Fritz-Haber-Institut Berlin

Combining conjugated organic with inorganic semiconductors opens up new possibilities for tailoring the properties and efficiency of optoelectronic devices by utilizing the advantages of each material class. Being able to tune the alignment of the frontier energy levels of hybrid inorganic/organic systems is essential to control their function. Employing molecular acceptor interlayers to tune the work function ($\phi$) of a metal and thus the energy level alignment between the metal and an organic semiconductor was demonstrated previously.

We now extend this concept to the polar surfaces of ZnO by using the strong molecular acceptor F4TCNQ. $\phi$ of bare ZnO surfaces was strongly increased by up to 3eV upon adsorption of a monolayer of the acceptor, as evidenced by photoelectron spectroscopy. In contrast to the strong inorganic-to-organic electron transfer found for F4TCNQ on metal surfaces, no peak associated with the LUMO below $E_F$, that would be expected for electron transfer from ZnO, is found in our experiments. DFT calculations suggest strong intramolecular charge rearrangement of F4TCNQ as mechanism for the $\phi$ increase on ZnO. The energy level alignment of sexiphenyl (6P) adsorbed on top of acceptor interlayers on ZnO is shown to be controlled via the $\phi$ changes.

DS 34.4 Thu 15:45 H 2032

**Charge Generation and Recombination in Perylene Solid State Dye-sensitized Solar Cells** — •Michael Meister, Ian A. Howard, Yoojin Kim, Henrike Wonneberger, Chen Li, Denis Andrienko, Klaus Müllen, and Frédéric Laquai — MPI für Polymerforschung Mainz

Perylene derivatives have attracted strong interest in replacing the commonly used Ru complexes as all organic sensitizers in solid state dye-sensitized solar cells (sDSCs), since they combine a strong absorption with reasonably good device efficiencies if used with Spiro-MeOTAD as solid state hole transporter. Here we present a photophysical study of promising perylene monoimide dyes (PMI) for sDSCs. By employing time resolved photoluminescence, quasi steady-state photoinduced absorption (PIA) and transient absorption (TA) spectroscopy in a broad visible and near-infrared spectral region on device-like structures, we gain insight into the mechanisms of charge generation and recombination. The results show that Li-TFSI, a commonly used additive, facilitates charge generation. As it turns out, reductive quenching, where hole transfer occurs prior to electron injection, plays a major role in charge generation for these dyes. However, we have evidence that initially separated charges are attracted back to the interface, likely due to the low dielectric constants, leading to increased recombination. This would be a major drawback of sDSCs. We suggest that to overcome this problem within the existing device configuration, exciton quenching must lead to a charge pair that is further spatially separated.

DS 34.5 Thu 16:00 H 2032

**Influence of interface dipoles on the open circuit voltage of polymer/PCBM based photovoltaic cells** — •Johannes Frisch[1], Stefanie Winkler[1], Jens Niederhausen[1], Patrick Amsalem[1], Antje Vollmer[2], Marcel Schubert[3], Dieter Neher[3], Eduard Preis[4], Ullrich Scherf[4], and Norbert Koch[1,2] — [1]Humboldt-Universität zu Berlin, Germany — [2]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany — [3]Universität Potsdam, Germany — [4]Bergische Universität Wuppertal, Germany

In heterojunction organic photovoltaic cells (OPVCs) the offset between the highest occupied molecular level of the donor and the lowest unoccupied molecular level of the acceptor (i.e., the photovoltaic gap) sets an upper limit for the open circuit voltage (Voc). Commonly, vacuum level alignment (VLA) at the donor/acceptor interface is assumed. In contrast, we found interface dipoles (ID) at such interfaces that affect the photovoltaic gap and therefore Voc. We report ultraviolet photoelectron spectroscopy measurements for three different polymer-PCBM heterojunctions, comprising the donors P3HT, poly(9,9'dioctylfluorene-alt-4,7-bis(2,5-thiendiyl)-2,1,3-benzothiadiazole) (PFTBTT) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT). The energy level alignment found experimentally for these heterojunctions are discussed in relation to the Voc achieved in corresponding OPVCs. In contrast to assumed VLA, the photovoltaic gap for the P3HT/PCBM junction is 0.15 eV wider due to the ID, and for PFTBTT/PCBM the photovoltaic gap is narrower by 0.15 eV.

DS 34.6 Thu 16:15 H 2032

**Effect of ionic strength on self-assembly and surface properties of oligoelectrolyte multilayers** — •Samantha Micciulla, Chloé Chevigny, and Regine v.Klitzing — Technische Universität Berlin, Deutschland

Polyelectrolyte multilayers are self-assembled systems which have found many applications since their introduction in the early nineties. Easiness of preparation and properties tunability have induced an increasing interest in the field of surface modification. This requires a deep understanding of their structural features and of the tools to con-

trol their response to different surrounding environments.
The effect of key parameters (pH, dipping time, concentration, functionality, charge density) has been largely studied. Our interest is now focused on the effect of chain length. Namely, we decided to go down to the oligomeric limit (30 monomers/chain) to test the achievement of layer-by-layer multilayer growth and understand how the molecular weight influences the resulting system.
The combination of optical (Ellipsometry) and acoustic (Atomic Force Microscopy (AFM) and Quarzt Crystal Microbalance with Dissipation (QCM-D) ) techniques offers an overall description of surface and rheological properties, pointing out the effect of ionic strength in solution on OEM self-assembly, as well as analogies and differences with their high molecular weight equivalents.

DS 34.7 Thu 16:30 H 2032

**Orientation of Non–Planar Molecules in thin Polycrystalline Layers from Infrared Ellipsometry Spectra – OFET and OPV materials** — •Jens Trollmann, Robert Lovrinčić, Carl Pölking, and Annemarie Pucci — Kirchhoff–Institut für Physik der Universität Heidelberg

The determination and control of molecular ordering in organic thin films is of particular interest for designing and improving production processes for organic field effect transistors (OFET) and organic photovoltaic (OPV) devices. By enhancing the molecular ordering in the conducting film performance of OFETs can be significantly improved. Furthermore the fill factor in organic solar cells can be increased by reorienting molecules. In this talk we show how to reliably conclude on the predominant molecular orientation in a thin film by a computation based comparison of infrared (IR) ellipsometric measurements with density functional theory calculations of vibrational eigenvalues and eigenvectors for a single molecule. To proof this concept we determined the anisotropic dielectric functions of two organic semiconductor thin films, ID583 and NDI-F, in the spectral range of 350 to 5000cm$^{-1}$. The approach is especially advantageous if applied to molecules with an anisotropic and non-planar structure forming X-ray amorphous layers with a preferred molecular orientation but an insufficient degree of long-range order for diffraction based methods. In such cases our analysis yields more accurate and significant results than achievable by only comparing ordinary and extraordinary refractive indices in the visible range. Funding by BMBF (Polytos) is gratefully acknowledged.

DS 34.8 Thu 16:45 H 2032

**Quantitative blend analysis of polymer/fullerene films via spectroscopic ellipsometry** — •Sebastian Engmann, Vida Turkovic, Harald Hoppe, and Gerhard Gobsch — Technische Universität Ilmenau, Institut für Physik, Experimentalphysik 1, Weimarer Straße 32, 98693 Ilmenau

Spectroscopic ellipsometry (SE) was used to determine the shape of fullerene inclusions in polymer/fullerene blends. The spatial distribution of the fullerene phase over the film depth is investigated, and we found evidence for spinodal de-mixing. The time development of the phase separations are investigated. Furthermore, ellipsometric measurements, in combination with refined optical modeling, are used to quantitatively describe the degree of spatial order of the polymer phase within polymer/fullerene blends.

DS 34.9 Thu 17:00 H 2032

**Temperature-sensitive swelling behavior of poly($N$-isopropylacrylamide) brushes characterized by in-situ infrared spectroscopic ellipsometry** — •Andreas Furchner[1], Dennis Aulich[1], Eva Bittrich[2], Sebastian Rauch[2], Petra Uhlmann[2], and Karsten Hinrichs[1] — [1]Leibniz-Institut für Analytische Wissenschaften – ISAS – e. V. — [2]Leibniz-Institut für Polymerforschung Dresden e. V.

Polymer brushes are very attractive material systems for biophysics and biochemistry. In aqueous environment, their surface properties show stimuli-responsive behavior on changes in, for example, temperature, pH, or solvent. This makes polymer brushes useful functionalized surfaces for applications like controlled protein and cell adsorption.

A suitable method for studying the film properties at the solid-liquid interface is infrared spectroscopic ellipsometry (IR-SE) in combination with a special in-situ cell. This allows to investigate the structural and chemical properties of polymer brushes in situ.

An important representative for temperature-sensitive polymer brushes is poly($N$-isopropylacrylamide) [PNIPAAm], which is of great technological interest owing to the phase transition at its lower critical solution temperature of 32°C. After an ex-situ characterization using an appropriate optical layer model, the swelling behavior of PNIPAAm brushes was investigated in neutral water at different temperatures around 32°C using in-situ IR-SE.

DS 34.10 Thu 17:15 H 2032

**Near-field Optical Imaging of Phase Separations in Organic Bulk Heterojunction Solar-cell Blends** — •Dai Zhang, Xiao Wang, and Alfred Meixner — IPTC, Uni Tübingen, Auf der Morgenstelle 15,Tübingen, Germany

Semiconductor Polymers and fullerenes are widely employed in organic solar cell as electronic donors and acceptors. To achieve high performance of the solar cell, the formation of bulk heterojunction (BHJ) morphology in the polymer and fullerenes blends at nm scale is critical [1].

We have recently demonstrated high resolution near-field spectroscopic mappings of organic semiconductor thin film and polymer:fullerene blend films [2-4]. From the simultaneously recorded morphology and spectroscopic information, the interplay among the blend film BHJ morphology, the local donor and acceptor distributions, and their photoluminescence (PL) quenching were discussed. The PL and Raman signals of the donor and acceptor have been probed at optical resolution of approximately 15 nm. In addition, the local degradation behaviours of the semiconductor donor molecule and the acceptor molecule were investigated.

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