

DS 18: Organic Thin Films I

Time: Wednesday 9:30–12:45

Location: CHE 91

DS 18.1 Wed 9:30 CHE 91

Structural and photophysical properties of a two dimensional J-aggregate: MePTCDI on KCl — ●CHRISTIAN MARQUARDT, ALEXANDER PAULHEIM, and MORITZ SOKOLOWSKI — Institute for Physical and Theoretical Chemistry, University of Bonn, Wegelerstraße 12, 53115 Bonn, Germany

The structural and photophysical properties of the organic dye molecule MePTCDI (N,N-dimethylperylene-3,4,9,10-bis(dicarboximide)) adsorbed on KCl(100) surfaces have been investigated by low energy electron diffraction (LEED), fluorescence (FL) and FL excitation spectroscopy (FLE). Similar to the model molecule PTCDA the monolayer of MePTCDI forms a commensurate $c(4 \times 4)$ brickwall structure on KCl. In this structure, the transition-dipole moments of the molecules are arranged in a head to tail conformation forming two-dimensional J aggregates. This results in a superradiant electronic transition in optical emission- and absorption-spectra with a pronounced 0-0-transition and a red shift with respect to the spectra of isolated molecules. We will present the results on MePTCDI and compare them to those of PTCDA on KCl [1].

[1] M. Müller et al., *J. Chem. Phys.* 139 044302 (2013).

DS 18.2 Wed 9:45 CHE 91

The frontiers of organic metal epitaxy: TTF-TCNQ thin film preparation on KCl(100) substrates — ●ALEXANDER MÄNZ, TOBIAS BREUER, and GREGOR WITTE — Molekulare Festkörperphysik, Philipps-Universität Marburg, Renthof 7, 35032 Marburg

The organic charge transfer complex Tetracyanoquinodimethane-Tetrathiafulvalene (TTF-TCNQ) exhibits interesting electronic properties and can be considered as a 1D organic metal. Although the epitaxial growth of TTF-TCNQ on alkali-halides is well known, the initial stages of film growth and thermal limitations of epitaxial ordering have yet not been studied systematically. While the crystallite size generally increases with substrate temperature upon growth, this process is limited by a sudden drop in the sticking coefficient. Alternatively, films at elevated temperatures were grown on seed layers that were deposited at low temperatures.

DS 18.3 Wed 10:00 CHE 91

Lead-phthalocyanine on graphite(0001): quantitative structural analysis via low-energy electron diffraction — ●MATTHIAS MEISSNER¹, ROMAN FORKER¹, TORSTEN FRITZ¹, YU WATANABE², NORIYAKI KAWAKITA², TAKASHI YAMADA², HIROYUKI S. KATO², and TOSHIKI MUNAKATA² — ¹Institute of Solid State Physics, Friedrich-Schiller University, Max-Wien-Platz 1, Jena 07743, Germany — ²Department of Chemistry, Graduate School of Science, Osaka University, Osaka 560-0043, Japan

Thin layers of organic molecules have attracted a wide interest since the dawn of organic electronics because the performances of those devices critically depend on interface properties. The system of lead-phthalocyanine (PbPc) on graphite has been studied intensively with scanning tunneling microscopy (STM) [1], photoemission electron microscopy PEEM [2], and two photon photoemission spectroscopy (2PPE) [3]. It was found that the electronic properties of the interface are coverage dependent [2]. Thus, for a comprehensive understanding of the results the structure of the PbPc layer is of interest. Therefore, a quantitative analysis of LEED measurements was carried out under varying conditions like temperature and coverage graphite single crystals and will be compared to STM, PEEM, and 2PPE results.

[1] R. Yamamoto et al., *Phys. Chem. Chem. Phys.* 14, 9601 (2012).

[2] I. Yamamoto et al., *Surf. Sci.* 602, 2232 (2008).

[3] I. Yamamoto et al., *Phys. Rev. B* 77, 115404 (2008).

DS 18.4 Wed 10:15 CHE 91

Investigation of Rubrene Thin Films on Graphite — ●CHRISTIAN UDHARDT¹, YU WATANABE², TAKASHI YAMADA², ROMAN FORKER¹, TOSHIKI MUNAKATA², and TORSTEN FRITZ¹ — ¹Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany — ²Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

The aim of our present work is to localize electronic states on organic thin film surfaces and associate them with film structures. The object

of study is a graphite surface covered with rubrene ($C_{42}H_{28}$), an organic dye from the class of polycyclic aromatic hydrocarbons (PAH). Previous studies of the graphite/rubrene interface with two-photon photoemission spectroscopy (2PPES) showed an enhanced, resonant excitation of a specific, unoccupied molecular orbital, which was labeled as Ln [*J. Phys. Chem. C* **116**, 5821 (2012)]. It is expected that the properties of the Ln excitation are influenced by an interaction with the image potential state of the graphite surface (IPS1). In this study, photoemission electron microscopy (PEEM) was used to localize the Ln excitation on the sample surface and gather further confirmations of the Ln-IPS mixing. Photon energy as well as film thickness dependence was investigated. In addition, the crystal structure at different thicknesses was characterized with low energy electron diffraction (LEED) and the light absorption behavior of the rubrene films was elucidated with differential reflectance spectroscopy (DRS).

DS 18.5 Wed 10:30 CHE 91

Interfaces between cobalt phthalocyanine and epitaxially grown ultrathin MnO films: Evidence for charge transfer. — ●MATHIAS GLASER¹, HEIKO PEISERT¹, HILMAR ADLER¹, UMUT AYGÜL¹, MILUTIN IVANOVIC¹, PETER NAGEL², MICHAEL MERZ², STEFAN SCHUPPLER², and THOMAS CHASSÉ¹ — ¹Universität Tübingen, Institut für Physikalische und Theoretische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany — ²Karlsruher Institut für Technologie, Institut für Festkörperphysik, 76021 Karlsruhe, Germany

The electronic properties of adsorbed transition metal phthalocyanines (TMPcs) on substrate surfaces are strongly affected by interactions at the interface [1,2]. Depending on the combination of the transition metal (TM) of the TMPc and the substrate, a charge transfer from the substrate to the TM may occur as observed, e.g. for CoPc/Ag(111) [2] and CoPc/Ni(111) [3]. Besides metals, transition metal oxide thin (TMO) films are promising substrates for applications of TMPcs - also in the view of a magnetic coupling between the molecules and the substrate. However, studies of these interfaces are rare. We performed photoemission and X-ray absorption experiments on the CoPc/MnO/Ag(100) system at different thicknesses of both oxide and organic films. The results are discussed in terms of local charge transfer processes across the interface.

[1] F. Petraki et al. *J. Phys. Chem. Letters* **1** (2010), 3380.

[2] F. Petraki et al. *J. Phys. Chem. C* **114** (2010), 17638.

[3] J. Uihlein et al. *J. Chem. Phys.* **138** (2013), 081101.

DS 18.6 Wed 10:45 CHE 91

Electronic and structural properties at the interface between a perylene di-imide-based molecule and gold — ●FRANCESCA CICCULLO¹, SABINE ANTONIA SAVU², ANTONIO CASSINESE¹, THOMAS CHASSÉ², and MARIA BENEDETTA CASU² — ¹CNR-SPIN and Department of Physics Science, University of Naples, Piazzale Tecchio 80, Naples, Italy — ²Institute of Physical and Theoretical Chemistry, Tübingen, Germany

Nowadays perylene di-imide derivatives are considered to be among the most promising n-type organic materials for high performance organic thin film transistors (OTFTs). However, the device behavior is strongly affected by interactions at the organic/substrate interface. A full understanding of these interactions is crucial to make these materials technologically appealing. In this work, we study N,N'-bis(n-ctyl)-x,y,dicyanoperylene-3,4,9,10-bis(dicarboximide) (PDI-8CN2) thin films deposited on Au(111) single crystals by using X-ray photoemission spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy, and atomic force microscopy (AFM). We focus on the investigation of morphology, molecular orientation, and electronic structure at the organic/metal interface. Our analysis reveals that the molecular bindings are perturbed when molecules come in direct contact with the gold surface, suggesting that PDI-8CN2 strongly interacts with gold atoms. At the state of the art, there is not any detailed comprehension of the PDI-8CN2/gold interface. We believe that our results are a relevant step forward to the full application of these materials in organic electronic devices.

Coffee break (15 min)

DS 18.7 Wed 11:15 CHE 91

The phthalocyanine heterojunction MnPc/F₁₆CoPc- An initial representative of a fascinating incipient material class?

— •SUSI LINDNER¹, BENJAMIN MAHNS¹, UWE TRESKE¹, MARTIN KNUPFER¹, RICO FRIEDRICH², TORSTEN HAHN², JENS KORTUS², FRANCISC HAIDU³, MICHAEL FRONK³, and DIETRICH R.T. ZAHN³ — ¹IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany — ²Institute of Theoretical Physics, TU Bergakademie Freiberg, Leipziger Str. 23, 09696 Freiberg, Germany — ³Physics Department/ Semiconductor Physics, Chemnitz University of Technology, Reichenhainer Str. 70, 09126 Chemnitz, Germany

Using x-ray photoelectron and x-ray absorption spectroscopy we demonstrate charge transfer at an interface between two transition metal phthalocyanines, MnPc and F₁₆CoPc, resulting in charged MnPc^{δ+} and F₁₆CoPc^{δ-}, species. Density functional theory calculations reveal that a hybrid state is formed between the two types of phthalocyanines, which causes this charge transfer. For the hybrid state the Mn 3d_{xz} interacts with the Co 3d_{z²} orbital leading to a two-level system.

Moreover, we have prepared mixed films out of this pair, which were characterized also by means of electron energy-loss spectroscopy. Our data reveal the formation of MnPc/F₁₆CoPc charge transfer dimers in analogy to the heterojunction. The electronic excitation spectrum of these blends is characterized by a new low energy excitation at 0.6 eV.

This project is supported by the DFG (KN 393/14).

DS 18.8 Wed 11:30 CHE 91

An electron energy-loss study of picene based charge transfer salts — •ERIC MÜLLER, BENJAMIN MAHNS, and MARTIN KNUPFER — IFW-Dresden, P.O.Box 270116, DE-01171 Dresden, Germany

The electronic excitations of coevaporated thin films of TCNQ/picene and F4TCNQ/picene have been investigated using electron energy-loss spectroscopy. We demonstrate that the investigated molecular pairs support charge transfer which result in new electronic excitation features at low energy. We discuss the character and localization of these low energy excitations. This work was supported by the DFG (KN393/14).

DS 18.9 Wed 11:45 CHE 91

Real-time *in situ* growth study of organic semiconductor heterostructures relevant for organic photovoltaics —

•CHRISTOPHER LORCH, RUPAK BANERJEE, JOHANNES DIETERLE, CHRISTIAN FRANK, HEIKO FRANK, SIMON WEIMER, ALEXANDER GERLACH, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen

The organic semiconductors (OSCs) sexithiophene (6T), diindenoperylene (DIP) and buckminsterfullerene C₆₀, when used as active layers in organic photovoltaic cells, have recently shown promising device parameters [1,2]. We have performed real-time growth studies of different combinations and heterostructures [3] of these compounds (*i.e.* material A on material B, mixtures A:B) at various substrate temperatures and deposition rates. Using *in situ* X-ray reflectivity and grazing incidence X-ray diffraction we investigated the growth and the resulting film structure of these compounds in the out-of-plane and in-plane direction, respectively. We present the results of the growth measured in real-time and the structure of the compounds under different preparation conditions as well as for different material combinations. Surprising findings lead to viable routes for tailoring the film structure which might help to improve device parameters.

[1] J. Wagner *et al.*, Adv. Funct. Mater., **20**, 4295 (2010)

[2] U. Hörmann *et al.*, Phys. Status Solidi RRL, **5**, 241 (2011)

[3] A. Hinderhofer *et al.*, ChemPhysChem **13**, 628-643 (2012)

DS 18.10 Wed 12:00 CHE 91

Vibrational properties of fluorinated rubrene in thin films

— •FALK ANGER¹, REINHARD SCHOLZ², ALEXANDER GERLACH¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen — ²Institut für Angewandte Photo-

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One possibility of tuning the electronic properties of organic molecules is the substitution of hydrogen end groups by fluorine. Vibrational spectroscopy can be used to obtain information about the conformation of the molecules as well as intermolecular coupling in thin films. Rubrene (C₄₂H₂₈) has been shown to be a suitable semiconductor for applications, for which numerous experimental efforts have been made. In this study, we present FT-IR and Raman spectra of thin films of partly (C₄₂H₁₄F₁₄) and completely (C₄₂F₂₈) fluorinated rubrene. We show that there is a very good agreement of the experimental vibrational spectra with state-of-the-art DFT calculations.

[1] F. Anger *et al.*, Appl. Phys. Lett. **102**, 013308 (2013)

[2] T. Breuer *et al.*, J. Phys. Chem. C **116**, 14491-14503 (2012)

DS 18.11 Wed 12:15 CHE 91

Diffraction Limited Polarized Raman Microscopy for Probing Nanoscale Structural Order — •XIAO WANG¹, KATHARINA BROCH², REINHARD SCHOLZ³, FRANK SCHREIBER², ALFRED J. MEIXNER¹, and DAI ZHANG¹ —

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Radially or azimuthally polarized doughnut laser beams (RPDB or APDB) are combined with topography studies of pentacene thin films, allowing to correlate Raman spectroscopy with intermolecular interactions depending on the particular pentacene modification. Polarization dependent Raman spectra of the C-H bending vibrations are resolved layer by layer within a thin film of approximately 20 nm thickness. The variation of the Raman peak positions indicates changes in the molecular orientation and in the local environment at different heights of the pentacene film. This method reveals the local structural order and the polymorph at different locations within the same pentacene thin film, depending mainly on its thickness: The first few monolayers grow in a thin film phase, but for larger film thicknesses, the morphology evolves towards the crystal bulk phase with a larger tilting angle of the pentacene molecules against the substrate normal.

DS 18.12 Wed 12:30 CHE 91

Real-time studies of the impact of intermolecular interactions and steric compatibility on structure-property relations in organic semiconductor blends — •KATHARINA BROCH, ALEXANDER GERLACH, CHRISTOPHER LORCH, JOHANNES DIETERLE, JIŘÍ NOVÁK, and FRANK SCHREIBER — Universität Tübingen, Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

An understanding of the structure-property relation in binary blends of organic semiconductors (OSCs) is relevant for device optimization as well as for fundamental research [1]. Due to possible pronounced transient effects, post growth studies are often not sufficient for a detailed characterization of these complex systems [2,3]. Using grazing incidence X-ray diffraction simultaneously with optical spectroscopy techniques we follow the growth of binary blends of the three OSCs pentacene, perfluoropentacene and diindenoperylene *in situ* in real-time. Comparing the results obtained for the different combinations, we find significant differences in the structure formation during growth of the mixed films as well as pronounced transient effects in the absorption spectra. We discuss these observations in the context of the competing effects of favourable intermolecular interaction and steric incompatibilities [4].

[1] A. Hinderhofer and F. Schreiber, ChemPhysChem **13**, (2012), [2] U. Heinemeyer *et al.*, Phys. Rev. Lett. **104**, (2010), [3] R. Forker and T. Fritz, Phys. Chem. Chem. Phys. **11**, (2009), [4] K. Broch *et al.*, J. Chem. Phys. **139**, (2013).