DS 19: Organic Interfaces (SYSA 6)

Time: Wednesday 14:30–17:30 Location: H 2013

Invited Talk DS 19.1 Wed 14:30 H 2013
Organometallic Nanojunctions Probed by Different Chemistries: Thermo-, Photo, and Mechanochemistry — •I. Stich[1,2], M. Konopka[1], R. Turansky[1], J. Reichert[3], N. L. Doltsinis[4], H. Fuchs[3], and D. Marx[4] — [1]Slovak Tech. Univ. (FEI STU), Slovakia — [2]Inst. of Phys., Slovak Acad. of Sci., Slovakia — [3]Uni. Muenster, Germany — [4]Ruhr-Uni. Bochum, Germany

Different methods of activation of chemical reactions are compared for organometallic nanojuctions. The study is based on density functional theory simulations. First we provide a comparison of thermal activation with mechanical activation, or mechanochemistry. Study of thiolate/copper junctions and interfaces provides evidence for vastly different reaction pathways and products. The differences are understood in terms of mechanical manipulation of coordination numbers and system fluctuations in the process of mechanical activation. Next we compare photo- and mechanochemistry. Azobenzene is an optically switchable molecule. Laser light is normally used to achieve molecular switching between the cis and trans isomers. We study azobenzene optomechanical switch which combines photo excitation with external pulling force to manipulate optical switching properties of the azobenzene molecule anchored to gold tips by thiolate bonds. We focus on the separation between ground (S0) and first excited (S1) singlet states. We observe a pronounced dependence of the S0-S1 separation on the applied strain. Furthermore we find that ground-state mechanochemistry alone can be used to achieve switching. For instance, mechanochemistry with modest applied forces leads to cis -> trans reisomerization.

DS 19.2 Wed 15:00 H 2013
Self-Assembled Monolayers of Azo-based molecular switches — Andrei Shaporenko[1], Mark Elbing[2], Alfred Blaszczyk[2], Violetta Ferri[3], Christian Grave[3], Giuseppina Pace[4], Carsten von Hänsich[2], Marcel Mayor[2,5], Paolo Samorì[4], Maria Anita Rampi[3], and •Michael Zharnikov[1] — [1]Angewandte Physikalische Chemie, Universität Heidelberg, D-69120 Heidelberg, Germany — [2]Forschungszentrum Karlsruhe GmbH, Institute for Nanotechnology, D-76021 Karlsruhe, Germany — [3]Dipartimento di Chimica, Università di Ferrara, I-44100 Ferrara, Italy — [4]Institut de Science et d'Ingénierie Supramoléculaires / CNRS UMR 7006 -Université Louis Pasteur, F-67000 Strasbourg, France — [5]Department of Chemistry, University of Basel, CH-4056 Basel, Switzerland

Two conjugated rod-like aromatic azo-compounds differing by molecular conformation (planar vs. twisted) and required free volume (upon assembly) have been synthesized. While the first compound forms tightly packed self-assembled monolayers (SAMs) on coinage metal substrates with a high degree of ordering, the second one packs more loosely giving less ordered films. However, independent of the package density, both compounds show very high yields of photoisomerization in SAMs, which are close to 100%. This result questions the common believe that isomerization in SAMs of azo-compounds can only be achieved efficiently, when enough free volume is available in the monolayer. We conclude that azo units incorporated in rigid molecular rods can be of potential interest in molecular electronic devices for applications such as switchable devices and high density data storage.

DS 19.3 Wed 15:15 H 2013
Structural and optical properties of self-organized surface structures on rubrene single crystals — •Rainer Stöhr[1], Gareth Beirne[2], Peter Michler[2], Jörg Wrachtrup[1], and Jens Pflaum[1] — [1]3. Physikalisches Institut, Univ. Stuttgart,Germany — [2]IHFG, Univ. Stuttgart, Germany

On the surface of rubrene single crystals high hole mobilities up to 15 cm^2/Vs have been observed making this material interesting for organic device applications. However, the optical properties of rubrene single crystals are yet barely analysed.

We present first structural and optical studies on sublimation grown rubrene single crystals with self-organized pyramidal microstructures on the (001) surfaces. From OMBD growth at various conditions we conclude on the stabilization mechanisms of these crystallographically aligned structures.

Measuring the time- and locally-resolved micro-photoluminescence at various positions on the structured rubrene (001) surface, four peaks could be identified in the wavelength range between 500nm and 900nm. The generated microstructures on the crystal surface enhanced the peak intensities by up to an order of magnitude. A clear dependence between structure size and enhancement could be shown. The results are carefully discussed by assigning these peaks to various exciton species with respect to studies currently reported in literature [1].

The DFG (projects WR28/5 and FOR 730) is acknowledged for financial support.

[1] H. Najafov *et al.*, PRL **96**, 056604 (2006)

DS 19.4 Wed 15:30 H 2013
Monitoring the crystallization process of nano-confined organic molecules — •Silvia Milita[1], Chiara Dionigi[2], Francesco Borgatti[2], William Porzio[3], Adina Lazar[2], Roberto Felici[4], Didier Wermeille[4], and Fabio Biscarini[2] — [1]CNR -IMM, Via Gobetti 101, I-40129 Bologna, Italy — [2]CNR -ISMN, Via Gobetti 101, I-40129 Bologna, Italy — [3]CNR-ISMAC Via E. Bassini 15, I-20133 Milano, Italy — [4]ESRF-bp 220, F-38043 Grenoble Cedex 9, France

In the recent years crystallisation behaviour upon nano-confinement has drawn extensive attention thanks to its potential application in nanotecnhologies. Production of new functional materials requires the understanding of crystallization phenomena in complex systems as emulsions, vescicles, micelles, air-water interfaces, ordered substrates. We will report on the dynamical X-ray diffraction investigation of the structure of organic semicondutor molecules in confined systems which are highly attractive for their application in electronic-optoelectronic devices as Organic Field Effect Transistor (OFET).

DS 19.5 Wed 15:45 H 2013
A molecular gas in two dimensions: Substrate-mediated repulsive interaction in an organic sub-monolayer film — •Christian Kumpf[1], Achim Schöll[1], Christoph Stadler[1], Ingo Kröger[1], and Eberhard Umbach[1,2] — [1]Universität Würzburg, Experimentelle Physik II, 97074 Würzburg — [2]Forschungszentrum Karlsruhe, 76133 Karlsruhe

The formation of the first molecular layer on a solid surface plays an important role for the growth behaviour of organic thin films. The first layer acts as a nucleus for further growth. It hence affects the structural properties of the entire film and consequently the electronic and optical properties. The development of the first layer depends strongly on the substrate bonding and the intermolecular interaction. Usually the latter is attractive due to van-der-Waals forces between the organic molecules thus resulting in island formation.

Here we report on an organic adsorbate system exhibiting repulsive intermolecular interaction mediated by the substrate. With increasing coverage Metal-Phthalocyanine (MePc) molecules continuously rearrange on a Ag(111) surface and – at all coverages – fill the entire surface homogenously. This is in contrast to discrete, well defined phase transitions which usually occur for such systems. Such unusual behaviour was found for Sn-, Cu- and TiOPc molecules. We report experimental results from spot-profile analysis-low energy electron diffraction, x-ray standing waves and photoelectron spectroscopy, and discuss an electronic donation/back-donation process as the fundamental origin of the intermolecular repulsion.

DS 19.6 Wed 16:00 H 2013
Influence of Intermolecular Bonding on Interface Barrier Formation of $ZnPcCl_8$ on Ag111 Observed by Kelvin Probe Force Microscopy — •Peter Milde[1], Christian Loppacher[2], Ulrich Zerweck[1], Mireille Mossoyan[2], and Lukas M. Eng[1] — [1]Institut für Angewandte Photophysik, Technische Universität Dresden — [2]Laboratoire de Matériaux et Microélectronique de Provence, Universités Paul Cézanne, Marseille

Phthalocyanines are a common class of organic dyes for applications in optoelectronic devices. Compared to the standard phthalocyanine, halogenated phthalocyanine shows a different and more complex bonding behavior. Within the first monolayer of $ZnPcCl_8$ on Ag111 distinct structural phases where observed, which can be attributed to the formation of 8, 4 and no intermolecular hydrogen-halogenide bonds[1].

FM-KPFM measurements reveal, that the bonding behavior does not only affect the structural ordering but also the electronic properties of the molecule and thus the interface barrier formation. Furthermore, a reversed sign of the contact potential change is found between ordered and disordered molecular layers.

Our results suggest, that for applications, in which single molecules or monolayers are used, it is crucial to exactly know the molecular arrangement at the interface, because both, the orientation and the intermolecular bonding, can strongly influence the interface barrier height.

[1] M. Abel et al., ChemPhysChem 7:82 (2006)

DS 19.7 Wed 16:15 H 2013

Direct Optical Observation of Charge Transfer between Metals and Epitaxial Organic Layers — •Roman Forker, Giovanni Pizzi, Christian Golnik, Thomas Dienel, and Torsten Fritz — Institut für Angewandte Photophysik, Technische Universität Dresden, 01062 Dresden, Germany

We investigate epitaxial mono- and multilayers of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) *in situ* on various metal surfaces by a variant of optical absorption spectroscopy. During film growth we observe pronounced changes in the spectra.

Unlike on insulating substrates, such as mica [1], the 1 ML spectra on Au(100), Au(111), and Ag(111) are broad and essentially featureless. Detailed theoretical work for PTCDA/Au(111) suggested significant molecular level broadening and interface electron density rearrangement induced by the metal proximity [2], which might be applicable to Ag as well despite reports of gap states in that case [3]. In the second ML on these metals, however, our spectra exhibit monomeric character similar to the first ML on mica, which indicates weak interaction with the underlying PTCDA layer. Besides the monomeric part of the 2 ML spectra on Au, a new feature at around 2.0 eV appears. By comparison to K-doped PTCDA on mica (where the anion shows up at 1.85 eV) and to semi-empirical calculations we reason that we optically probe cationic PTCDA in the partly charged second ML on Au.

[1] H. Proehl *et al.*, Phys. Rev. Lett. **93** (2004), 097403.
[2] H. Vázquez *et al.*, Europhys. Lett. **65** (2004), 802.
[3] Y. Zou *et al.*, Surf. Sci. **600** (2006), 1240.

DS 19.8 Wed 16:30 H 2013

Hole injection barrier optimization at ITO/organic interfaces modified with strong molecular acceptors — •Ralf-Peter Blum[1], Benjamin Bröker[1], Steffen Duhm[1], Antje Vollmer[2], Ralph Rieger[3], Hans Joachim Räder[3], Klaus Müllen[3], Jürgen P. Rabe[1], and Norbert Koch[1] — [1]Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, D-12489 Berlin, Germany — [2]Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH, D-12489 Berlin, Germany — [3]Max Planck Institut for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

The hole injection barriers at interfaces between N,N'-diphenyl-N,N'-bis(1-naphthyl)-1-1'biphenyl-4,4"diamine (α-NPD) and chemically modified ITO substrates have been studied by ultraviolet photoelectron spectroscopy (UPS). A decreased hole injection barrier was achieved by an appropriate arrangement of oriented dipoles, formed by chemisorption of strong electron acceptors, i.e., tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) or hexacyanohexaazatriphenylene [HAT-(CN)]. In both cases thin acceptor layers induce coverage dependent work function shifts of more than 1 eV, thereby modifying the barrier to hole injection into α-NPD by up to 0.4 eV. We observed a linear dependence of the hole injection barrier versus the work function of modified ITO substrates. However, we find constant hole injection barriers for substrate work functions greater than 5.1 eV caused by localized states at the interface. This work is financially supported by the European Community project "IControl" (EC-STREP-033197).

DS 19.9 Wed 16:45 H 2013

Molecular band offsets and Charge Neutrality Levels at organic interfaces — •Héctor Vázquez[1], Mads Brandbyge[1], Antti-Pekka Jauho[1], and Fernando Flores[2] — [1]MIC-Department of Micro and Nanotechnology, Technical University of Denmark, DTU, DK-2800 Lyngby, Denmark. — [2]Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Spain.

We present a theoretical method to calculate the energy level alignment at interfaces of organic semiconductors based on the Charge Neutrality Levels (CNLs). The CNLs act as the electronegativity or effective Fermi level of the organic material at the interface.

We calculate the CNL position from the isolated organic molecule, rather than at the interface. We perform a DFT calculation of the molecule and consider energy corrections associated with the addition or removal of an electron; these result in shifts of the molecular levels, increasing the molecular gap with respect to DFT. The CNL position is calculated from the branch point of the molecular Greens function. The screening parameters at the interface, which also affect molecular level offsets, can be estimated from the static dielectric functions of the organic materials.

We have performed this analysis for several organic molecules, including, bathocuproine, Alq3 and hexaazatrinaphthylene derivatives, comparing induced dipoles and interface properties with experiment. Our work suggests that, at interfaces where the details of the interaction are not important, the CNL picture represents a general and intuitive model for understanding organic semiconductor interfaces.

DS 19.10 Wed 17:00 H 2013

Manipulation and Imaging of Aromatic Organic Molecules with Atomically Sharp Tips: The Last Atom Matters — Nicolae Atodiresei[1], Vasile Caciuc[2], Hendrik Hölscher[2], and •Stefan Blügel[1] — [1]Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Center for NanoTechnology (CeNTech), University of Münster, Heisenbergstr. 11, 48149 Münster, Germany

The manipulation and imaging of organic molecules is of high interest for the development of nanoelectronic devices. Based on *ab initio* calculations we simulated how an aromatic organic molecule like benzene adsorbed on a Cu(110) surface can be imaged and mechanically manipulated in non-contact atomic force microscopy using two types of atomically sharp tips. A clean Silicon tip pushes the Benzene molecule from one adsorption site to another and can therefore be used for *lateral* manipulation processes. On the other hand, a Copper terminated tip binds to the benzene molecule lifting it from the Cu surface, thus leading to a *vertical* manipulation of this molecule.

DS 19.11 Wed 17:15 H 2013

Structure and electronic properties of mercaptoalkyl-ferrocenes, studies by STM — Lars Müller-Meskamp[1], •Silvia Karthäuser[1], Melanie Homberger[2], Ulrich Simon[2], and Rainer Waser[1] — [1]Institute of Solid State Research, Research Center Juelich GmbH, 52425 Juelich, Germany — [2]Institute of Inorganic Chemistry, RWTH-Aachen, Landoltweg 1, 52056 Aachen, Germany

The ability to access and use the electronic properties of individual molecules together with the inherent capability of self-organization, promises new possibilities for future microelectronic circuits. On this way the behavior of electroactive molecules with redox-centers, like ferrocenes, is especially interesting. Here we report on the structure and electronic properties of mercaptoalkyl-ferrocene self-assembled monolayers, studied by STM and STS. The molecular structures of pure full coverage and of submonolayer-coverage phases of different mercaptoalkyl-ferrocenes in mixed layers with alkanethiols on Au(111) are resolved. The ferrocenes form striped surface pattern resulting in equally spaced rows of ferrocene moieties. The obtained nanoscale lattice of functional groups offers an interesting potential for patterning of periodic structures. Besides this the electronic behavior of mercaptoalkyl-ferrocenes is studied by STS, which allows a direct determination of the decay constant of the ferrocene moiety.

References: [1] L. Müller-Meskamp et al., JoP: CS 61, 852 (2007). [2] L. Müller-Meskamp et al., PSS(a) 203, 1448 (2006).