O 26: Organic-inorganic hybrid systems and organic films III

Time: Tuesday 10:30–13:00 Location: MA 042

O 26.1 Tue 10:30 MA 042

Self-assembly and metal coordination of 1,4-bis(1h-tetrazol-5-yl)benzene on Ag(111) in vacuo — •Peter Knecht[1], Anthoula Papageorgiou[1], Bodong Zhang[1], Joachim Reichert[1], Nithin Suryadevara[2], Svetlana Klyatskaya[2], Mario Ruben[2], and Johannes Barth[1] — [1]Physics Department E20, Technical University of Munich, Garching D-85748, Germany — [2]Institute for Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen D-76344, Germany

A phenyl functionalized with two tetrazole moieties at para positions is promising for magnetically active metal-organic coordination networks [1]. This route can be potentially extended to polyphenyls, which would result in linear tuning of the separation of the magnetically active metal atoms in the network [2-3]. En route to prepare such surface supported networks, we investigated the self-assembly and metal coordination of 1,4-bis(1h-tetrazol-5-yl)benzene on the atomically smooth Ag(111) surface under UHV conditions. The molecular layers are prepared by organic molecular beam epitaxy. Scanning tunneling microscopy and X-ray photoelectron spectroscopy are used to investigate the assembly of the molecules and their chemical state. The coordination of the tetrazole moieties with the native Ag adatoms is observed after annealing to 160 °C, whereas coordination with magnetically active Fe3+ atoms is achieved upon codeposition and annealing to ~120 °C.

[1] Yan, Zheng et al. Chem. Commun. 48 (2012) 3960
[2] Schlickum, U. et al. Nano Lett. 7 (2007) 3813
[3] Kühne, Dirk et al. JACS 131 (2009) 3881

O 26.2 Tue 10:45 MA 042

Surface-activated spin-crossover of a low-spin Fe(II) complex probed by NEXAFS — •Sebastian Rohlf[1], Benedikt Flöser[2], Manuel Gruber[1], Matthias Kalläne[1], Simon Jarausch[1], Jan Grunwald[2], Felix Tuczek[2], and Kai Rossnagel[1] — [1]Institut für Experimentelle und Angewandte Physik, Universität Kiel, 24098 Kiel, Germany — [2]Institut für Anorganische Chemie, Universität Kiel, 24098 Kiel, Germany

The controlled spin-state manipulation of Fe(II) coordination complexes by external stimuli is associated with pronounced changes in the electronic, magnetic, and structural properties and may be implemented in future spintronic devices. To preserve the functionality of spin-crossover (SCO) complexes in device-like environments, where the molecules are typically fragile, such as in direct contact to a metallic surface, their sterical stability needs to be enhanced. However, this generally leads to a decrease of the transition temperature below which bi-directional spin switching is possible. Here, we present a near edge X-ray absorption fine structure (NEXAFS) spectroscopy study of the stabilized SCO derivative $\mathrm{Fe(PyPyr(CF_3)_2)_2(phen)}$ adsorbed on metallic surfaces. SQUID measurements showed that the high-spin state appears to be fully suppressed in the bulk complex. In contrast, our NEXAFS results indicate that in thin films the SCO functionality is activated in the vicinity of the surface. At low temperatures and during laser light irradiation, the studied complex exhibits an almost complete low-spin to high-spin state transition, which has not been observed for other bulk low-spin complexes so far.

O 26.3 Tue 11:00 MA 042

Mixed aliphatic self-assembled monolayers with embedded polar group — •Eric Sauter[1], Jean-Francois Morin[2], and Michael Zharnikov[1] — [1]Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — [2]Departement de Chimie and Centre de Recherche sur les Materiaux Avancees (CERMA), Universite Laval, Quebec QC Canada G1 V 0A6

We studied structure, molecular orientation, morphology, and electrostatic properties of mixed self-assembled monolayers (SAMs) comprised of alkanethiolates with the dipolar ester group embedded into the alkyl backbone at two opposite orientations. The packing density and molecular orientation in these films were found to be similar to those of the "parent" single-component monolayers. Applying X-ray photoelectron spectroscopy (XPS) as a morphology tool, we could estimate that the mixed SAMs represent homogeneous intermolecular mixtures of both components, down to the molecular level, excluding existence of "hot spots" for charge injection. The analysis of the C 1s XPS spectra and the work function data suggests that the composition of the mixed SAMs fully mimicked the mixing ratio of both components in the solutions from which these SAMs were prepared, which suggests a minor role of the dipole-dipole interaction in the overall balance of the structure-building forces. Varying this composition, work function of the gold substrate could be tuned linearly, in controlled fashion within a 1.1 eV range, at the persistent chemical composition of the SAM-ambient interface.

O 26.4 Tue 11:15 MA 042

Adsorption energies of aromatic molecules from quantitative TPD — Stefan R. Kachel[1], Benedikt P. Klein[1], Janika Hochstrasser[1], Martin Schmid[1], Steffen Seiler[2], Bernd Meyer[2], and •J. Michael Gottfried[1] — [1]Fachbereich Chemie, Philipps-Universität Marburg, Germany — [2]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Arguably the most important single parameter for the quantitative characterization of metal-organic interfaces is the adsorption energy, which can be determined by precision temperature-programmed desorption (TPD) experiments via the desorption activation energy. Such energies represent valuable benchmark data for comparison with computational studies and are important prerequisites for the further rational improvement of organic electronic devices, in which metal-organic interfaces occur at the contacts between electrode and semiconductor. Since many typical organic semiconductors are based on aromatic hydrocarbon backbones, we focus here on benzene and other aromatic model compounds and study their interactions with the (111) surfaces of Cu, Ag and Au. An advanced TPD setup with a cryoshroud housing around the mass spectrometer enables us to suppress desorbing molecules without a direct line-of-sight path between the surface and the ion source. The precise desorption energies obtained by detailed analysis will be compared with previous experimental and theoretical results.

O 26.5 Tue 11:30 MA 042

A simple modification of Grimme's D3 density functional dispersion correction scheme for more accurate adsorption energies of organic molecules on surfaces — •Steffen Seiler[1], Stefan Renato Kachel[2], Janika Hochstrasser[2], J. Michael Gottfried[2], and Bernd Meyer[1] — [1]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [2]Fachbereich Chemie, Philipps-Universität Marburg, Germany

The semiempirical D3 dispersion corrections of Grimme [1] to density functional theory calculations are highly successful for predicting structural and energetical properties of molecular aggregates. However, when it comes to the adsorption of molecules on surfaces of solids, often a significant overbinding is observed. We will present a simple modification of the D3 scheme based on ideas of the older D2 version that significantly reduces the overbinding. The improvement will be demonstrated by comparing calculated binding energies of aromatic molecules and porphyrins on metal and oxide surfaces with recent data from state-of-the-art TPD experiments.

[1] S. Grimme, et al., J. Chem. Phys. **132** (2010) 154204.

O 26.6 Tue 11:45 MA 042

How Doping Influences the Nature of Charge Transfer at ZnO/F4TCNQ Interfaces — •Simon Erker and Oliver T. Hofmann — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

At inorganic/organic interfaces, charge transfer occurs in different forms depending on the nature of the substrate. On metals, where the adsorbate often hybridizes with the substrate, hybrid bands a formed. These lead to a uniform, fractional charging of the organic monolayer. In contrast, on insulating and inert substrates, charge is transferred as integer electrons, which leads to the coexistence of charged and neutral molecules on the surface. In this contribution, we study the charge distribution of F4TCNQ on ZnO using hybrid density functional theory. ZnO is particular interesting substrate, which allows to study the transition between these two mechanisms. Experimentally, it can be produced with high purity or doped until metallic conductance.

Moreover, while the 000-1 surface is inert due to the presence of a hydrogen overlayer, the 10-10 surface exposes surface Zn atoms that can hybridize with organic adsorbates. Employing a recently developed approach to incorporate doping and the effect of long-ranged band bending into our calculations, we investigate the transition between fractional and integer charging as function of the doping concentration for the two different surfaces.

O 26.7 Tue 12:00 MA 042

F4-TCNQ and F6-TCNNQ Adsorbed on H-Si(111): Structure and Work-Function Changes. — •Haiyuan Wang, Svenja Janke, Sergey Levchenko, Mariana Rossi, and Matthias Scheffler — Fritz Haber Insitute of the Max Planck Society, Berlin, Germany

The tunability of hybrid inorganic/organic materials makes them promising candidates for more efficient photovoltaic and electronic devices. Even though the electronic properties of these materials critically depend on the structure of the interface, the latter is often poorly understood or characterized. Here we address model hybrid systems composed by the efficient electron acceptor molecules F4-TCNQ and F6-TCNNQ adsorbed on hydrogenated Si(111) surfaces [H-Si(111)]. We demonstrate how structural variations can lead to different electronic properties through a characterisation of these systems with density-functional theory, employing the HSE06 functional augmented with many-body van-der-Waals corrections [1]. We present exhaustive structure searches that show that F4-TCNQ and F6-TCNNQ lie flat on H-Si(111) at low coverages and become negatively charged. Interestingly, increasing the coverage to around 25% leads to a more stable structural motif with molecules standing at an angle to the surface. This motif is necessary to explain the work-function increase observed in experiment for the same system, which are performed in collaboration with T. Shultz and N. Koch (HU Berlin). This work is supported by SFB-951 project (HIOS).

[1] A. Ambrosetti et al., J. Chem. Phys. 140, 18 (2014).

O 26.8 Tue 12:15 MA 042

Structure and Property Prediction of Tetracene and Pentacene at H:Si(111): A Conceptual Picture for Hybrid Inorganic/Organic Systems — •Svenja Janke[1,2], Haiyuan Wang[1], Volker Blum[2], Sergey Levchenko[1], Mariana Rossi[1], and Matthias Scheffler[1] — [1]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [2]Duke University, Durham, USA

Hybrid organic inorganic systems allow to combine the properties of organic and inorganic substances and hence open up a wide field for new materials with tunable properties. In particular, the organic compound offers a large range of functionalities and can be designed to be environmentally benign. As a key example of aromatic molecule-interface systems, we present a first-principles structure search and electronic-property investigation of pentacene (Pc) and tetracene (Tc) adsorbed at the hydrogenated Si(111) surface. The adsorption of single molecules is explored at different thin film coverage conditions with a structure search routine that includes grid- and random-structure search elements. This enables us to identify the most favorable orientation of the acene molecules and, using hybrid functionals, to investigate the level alignment between the organic and inorganic compounds with respect to the possibility of charge transfer: Single Tc and Pc molecules prefer to lie flat on the surface. For both organic molecules, the HOMO lies at the top of the valence band maximum allowing at best little charge transfer. For increasing coverage, we expect a transition to a dense geometry of standing molecules. This work is part of SFB-951 (HIOS).

O 26.9 Tue 12:30 MA 042

Optoelectronic Properties of Hybrid Systems of Inorganic Semiconductors and the Organic Semiconductor α-Hexathiophene — •Hannah Schamoni, Oliver Bienek, Felix Eckmann, and Martin Stutzmann — Walter Schottky Institut und Physik-Department, Technische Universität München, Am Coulombwall 4, 85748 Garching, Deutschland

The combination of organic and inorganic semiconductors is one promising approach towards new materials for applications like solar cells and light emitting devices, as they open up the possibility to benefit from the advantages of both material types. In order to identify the most promising hybrid systems, a detailed knowledge of the properties of the organic/inorganic interface is essential. In this work, thin films of the organic semiconductor α-hexathiophene are deposited on Si and SiC in an organic molecular beam deposition (OMBD) setup. The resulting hybrid systems are characterized amongst others by current-voltage and Kelvin Probe Force Microscopy measurements. On that basis, we discuss the influence of the choice of inorganic material on the optoelectronic properties of the hybrid systems. For example, the current-voltage output characteristics of the heterojunctions are found to depend on the doping type and strength of the inorganic substrate.

O 26.10 Tue 12:45 MA 042

Protoporphyrin IX functionalized GaN surfaces as a model system for photocatalytic hybrid devices — Felix Eckmann, •Jennifer Padberg, and Martin Stutzmann — Walter Schottky Institut und Physik-Department, Technische Universität München, Am Coulombwall 4, 85748 Garching

Efficient photocatalytic conversion of carbon dioxide into solar fuels constitutes an attractive option to reduce the problem of energy storage present in today's renewable energy technology. Although extensive research efforts have already been made, the conversion efficiencies and long-term stability of current devices are still far from feasible for large scale applications. In the current work, gallium nitride surfaces functionalized with protoporphyrin IX self-assembled monolayers are investigated as a model system to gain insights into future photocatalytic devices using similar functionalized surfaces. Sulfo-NHS activated protoporphyrin IX monolayers were created by adsorption from solution or by Langmuir-Blodgett deposition onto aminopropyltriethoxysilane-functionalized gallium nitride surfaces in order to create a chemisorbed monolayer. Thermally programmed desorption studies are carried out to gain information on the binding energy of the molecules on the surface. Polarized FTIR and AFM studies give indications on molecule orientation and layer morphology. Additionally, fluorescence spectroscopy and optical absorption spectroscopy highlight the changing optical properties accompanied by the transition from solved molecules to a chemisorbed solid monolayer.