

## O 45: Organic-Inorganic Hybrid Systems and Organic Films

Time: Tuesday 18:30–20:30

Location: P1A

O 45.1 Tue 18:30 P1A

**Preparation of well-defined metal films on top of self-assembled monolayers** — ●MICHAEL ZHARNIKOV — Applied Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Self-assembled monolayers (SAMs) can be potentially used as ultrathin insulating dielectric layers or intermediate films in future electronic and spintronic devices. Whereas the bottom electrode in such devices is provided by the metal substrate, the top electrode should be prepared in controlled fashion at the SAM-ambient interface. Regrettably, this is a non-trivial task, since the metal atoms deposited onto the SAM-ambient interface do not stay there, but penetrate into the monolayer and diffuse to the metal substrate. Here I discuss three new approaches to suppress the above penetration and diffusion, taken nickel, as a test adsorbate. The first approach relies on irradiation-induced cross-linking of a thiol-substituted aromatic SAM. Whereas 2D-polymerization of such a SAM prevents penetration of the metal atoms into the monolayer, the thiol groups at the SAM-ambient interface serve as nucleation centers for the growing "top" metal film. The second approach, relying on SAMs of perfluoroterphenyl-substituted alkanethiols, utilizes a chemical reaction between the SAM constituents and adsorbate atoms. Finally, the penetration of deposited metal atoms into a SAM can be nearly completely inhibited by preliminary formation of palladium-chloride seeding layer at the SAM-ambient interface. The Pd atoms in the seeding layer serve as nucleation centers for the growing metal film while the Cl atoms perform as surfactants.

O 45.2 Tue 18:30 P1A

**Assembly of metal-organic complexes on solid support: design, properties, and applications** — ●MICHAEL ZHARNIKOV — Applied Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Transition metal complexes allow a high degree of molecular design flexibility through symmetry considerations and ligand architecture, which can be explored for the fabrication of ordered molecular and oligomer assemblies through bottom-up approach. Here I describe the preparation of such assemblies, viz. monocomponent and multicomponent coordination-based monomolecular, dimer, trimer, and oligomer films on siloxane-based templates by wet-chemical layer-by-layer deposition process. In these films optically-rich metal polypyridyl complexes having pendant pyridine groups (so called metallo-ligands) were combined with a coinage metal (copper or silver) that acted as a linker between the polypyridyl complex moieties. The properties of the above assemblies were studied in detail by suitable combination of several complementary experimental techniques. Examples of potential applications are given, including volatile memory devices, logical gates, high-selectivity sensors, systems for photoinduced DNA cleavage, and catalytically active surfaces.

O 45.3 Tue 18:30 P1A

**Transition from fractional to integer charge transfer at the inorganic-organic interface via alloying** — ●ELISABETH WRUSS, EGBERT ZOJER, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

When investigating interfaces consisting of an organic layer on an inorganic substrate, two different types of charge transfer toward the adsorbate can arise. Either all molecules get fractionally charged or the charge localizes on individual molecules. While fractional charge transfer appears mostly in case of pristine metals, coexistence of charged and uncharged molecules occurs on more unreactive surfaces. In this work we address the transition between these two situations via DFT simulations. Starting with an acceptor molecule on a metallic substrate, we continuously decrease the density of states at the Fermi edge via alloying of the substrate until an integer charge transfer situation is established. By investigating the system at different alloying concentrations we analyze the properties of this transition. As a model system we have chosen the acceptor molecule TCNE on copper, which can be converted into the semiconducting cupric oxide Cu<sub>2</sub>O. To adequately model the charge transfer within DFT, large unit cells containing a sufficient number of molecules and hybrid functionals are needed. Therefore these simulations are computationally very demanding. This is one of the main reasons why the possibility of integer charge transfer

has often been neglected in computational studies, although its consideration can be of uttermost importance for the understanding of the electronic properties of many inorganic-organic interfaces.

O 45.4 Tue 18:30 P1A

**A monolithic setup for preparation of thin films and time-resolved multidimensional spectroscopy at the nanoscale** — ●SEBASTIAN PRES<sup>1</sup>, BERNHARD HUBER<sup>1</sup>, EMANUEL WITTMANN<sup>2</sup>, LYSANNE DIETRICH<sup>1</sup>, JULIAN LÜTTIG<sup>1</sup>, VICTOR LISINETSII<sup>1</sup>, MATTHIAS HENSEN<sup>1</sup>, EBERHARD RIEDLE<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität, Oettingenstraße 67, 80538 München, Germany

We present a versatile experimental setup for preparing thin organic and inorganic films which can be characterized by low energy electrons (LEEM, LEED). To investigate the nature of energy transport processes between individual molecules or inside large heterogeneous structures, we want to combine the femtosecond time resolution of coherent 2D spectroscopy with nanoscale selectivity: Instead of measuring optical diffraction-limited light fields, we detect photoemitted electrons with spatial resolution <10 nm using aberration-corrected photoemission electron microscopy (AC-PEEM). The sub-30 fs optical excitation is generated by a two-branch noncollinear optical parametric amplifier (NOPA) featuring wide spectral tunability from the NIR to the UV range at repetition rate up to 1 MHz. Here we demonstrate the tunability of the laser system from 230 nm - 900 nm at simultaneously high pulse compressibility down to 20 fs. Using collinear four-pulse sequences we want to explore well-defined organic-inorganic hybrid systems by time-resolved multidimensional spectroscopy.

O 45.5 Tue 18:30 P1A

**How K-doping affects the properties of DBP monolayers on Ag(111)** — ●TINO KIRCHHÜBEL, FELIX OTTO, MARCO GRUENEWALD, ROMAN FORKER, and TORSTEN FRITZ — Institute of Solid State Physics, Friedrich Schiller University Jena, Germany

Doping is a suitable tool to tune the electronic properties and the absorption of organic semiconductors for the purpose of specific technical applications. Recently, tetraphenyldibenzoperiflanthene (DBP), which is applicable as a donor or acceptor for other molecules,<sup>1</sup> was used as a component of optoelectronic devices. Here, we investigate how doping affects DBP itself, by studying the interplay between the optical and electronic properties, as well as the structure of potassium doped epitaxial DBP thin films on Ag(111). For DBP sub-monolayers several different laterally ordered structures depending on the local K:DBP stoichiometry are observed using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). As concluded from ultraviolet photoelectron spectroscopy (UPS) experiments, an electron transfer from potassium to DBP is achieved. Our differential reflectance spectroscopy (DRS) measurements show that this lowest unoccupied molecular orbital (LUMO) filling leads to tremendous alterations of the molecular absorption and even reduces the molecule-substrate interactions significantly. The optical fingerprints of DBP anions with reduced hybridization to the silver surface and dianions, which are rather effectively decoupled from the substrate, are identified by comparison to optical spectra of K-doped DBP films on inert mica.

[1] A. N. Bartynski *et al.*, *J. Phys. Chem. C*, **2016**, *120*, 19027.

O 45.6 Tue 18:30 P1A

**Ordered superstructures of a molecular electron donor on Au(111)** — ●ALEXANDER MEHLER<sup>1</sup>, TINO KIRCHHÜBEL<sup>2</sup>, NICOLAS NÉEL<sup>1</sup>, ROMAN FORKER<sup>2</sup>, TORSTEN FRITZ<sup>2</sup>, and JÖRG KRÖGER<sup>1</sup> — <sup>1</sup>Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany — <sup>2</sup>Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany

The molecular donor tetraphenyldibenzoperianthene (DBP) exhibits coverage-dependent superstructures on Au(111). At submonolayer coverages the molecules align parallel to each other. They arrange in row-like structures, which exhibit a nearly rectangular primitive unit cell. The closed molecular monolayer is characterized by a herringbone-type DBP arrangement spanned by an almost square unit cell con-

taining two molecules. Both superstructures simultaneously occur in a narrow coverage range close to completion of the molecular monolayer. Structural properties were consistently probed in real and reciprocal space by scanning tunnelling microscopy and low-energy electron diffraction, respectively.

O 45.7 Tue 18:30 P1A

**Manipulation of H<sub>2</sub>Pc tautomerization by multi-atom structures** — ●MARKUS LEISEGANG<sup>1</sup>, JENS KÜGEL<sup>1</sup>, ANDREAS KRÖNLEIN<sup>1</sup>, MARKUS BÖHME<sup>1</sup>, and MATTHIAS BODE<sup>1,2</sup> — <sup>1</sup>Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Wilhelm Conrad Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Recent scanning tunneling microscopy (STM) studies showed that the switching behavior of hydrogen protons between different molecular sites, a so-called tautomerization, can be influenced by a molecule-substrate symmetry mismatch [1] or by the proximity of a single atom [2]. Here, we will show how the controlled switching behavior of a single H<sub>2</sub>Pc molecule and its dehydrogenated form can be modified by nanostructures assembled in an atom-by-atom process. Towards this goal we developed an experimental procedure that allows for the highly controllable release of single atoms from silver STM tips onto a Ag(111) surface. Manipulating these adatoms facilitates the creation of various molecular environments that reduce or amplify the tautomerization processes.

[1] J. Kügel *et al.*, *ACS Nano* (DOI: 10.1021/acs.nano.6b05924).

[2] T. Kumagai *et al.*, *Nat. Chem.*, **6**, 41-46 (2014).

O 45.8 Tue 18:30 P1A

**Adsorption and desorption of water on oligo(ethylene glycol) substituted alkanethiolate monolayers** — ●MUSTAFA SAYIN<sup>1</sup>, ALEXEI NEFEDOV<sup>2</sup>, and MICHAEL ZHARNIKOV<sup>1</sup> — <sup>1</sup>Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — <sup>2</sup>Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

We studied kinetics and thermodynamics of the water adsorption and desorption as well as wetting and nucleation behaviors of water on a series of model organic surfaces, formed by oligo(ethylene glycol) substituted alkanethiolate (OEG-AT) self-assembled monolayers. The ultimate goal of the study was to get a better understanding of the mechanism behind the inertness of poly(ethylene glycol) and OEG-based organic surfaces with respect to protein adsorption and biofouling. The kinetic and thermodynamic parameters were studied by thermal desorption spectroscopy. Two adsorbate phases with different parameters and behavior were observed, viz. the interfacial and hydration phase. The bonding character of the hydration phase as well as the structure and morphology of the interfacial phase were investigated by high resolution X-ray photoelectron spectroscopy and near edge X-ray absorption fine structure spectroscopy.

O 45.9 Tue 18:30 P1A

**Computational Phase Diagram Prediction for Organic Monolayers on Metal Substrates** — ●LUKAS HÖRMANN, MICHAEL SCHERBELA, VERONIKA OBERSTEINER, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

Monolayers of organic molecules on inorganic substrates often show rich polymorphism with diverse structures in differently shaped unit cells. Determining the different commensurate structures and their epitaxy matrices from first principles is far from trivial due to the large number of possible polymorphs.

We pursue a novel approach based on coarse-graining the potential energy surface and applying machine learning to efficiently determine the energetically most stable structures. First the adsorption geometries of isolated molecules as well as all possible unique super cells of the substrate are determined. Then all configurations are generated by combining each adsorption geometry with every super cell. For a subset of configurations adsorption energies are determined using dispersion-corrected DFT. This subset serves as training data for a machine learning algorithm, that allows us to predict the adsorption energies for all configurations. Configurations with an adsorption energy below a predefined energy threshold are then probed using DFT.

We demonstrate the capability of our approach for TCNE (tetracyanoethene) on Cu(100) and Naphthalene on Cu(111). We determine the adsorption energies for a large number of polymorphs and compare the results to the experimentally obtained phase diagram.

O 45.10 Tue 18:30 P1A

**Investigating the stability of thiolates and selenolates on Au(111) using density functional theory** — ●GIULIA NASCIMBENI, ELISABETH VERWÜSTER, and EGBERT ZOJER — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8020 Graz, Austria

Considering that chemical and physical properties of sulfur and selenium are very similar, self-assembled monolayers (SAMs) of selenoles are frequently used as an alternative to the thiole ones, often achieving superior film properties. In this work we study the stability of thiole and selenole based SAMs on Au(111) using dispersion-corrected density functional theory. As test systems we consider both aromatic and aliphatic SAMs, which have been experimentally intensively characterized [1, 2]. Our main goal is to gain fundamental insight into the relative stabilities of the bonds between the metal and the docking groups and between the docking groups and the SAM backbones. In order to account for the contributions of zero point energy and thermally activated vibrations, we also calculated the vibrational properties of the extended metal-SAM interfaces and of the individual components of the system of interest.

[1] Ossowski *et al.*, *ACS Nano*, 2015, **9**, 4508.

[2] Ossowski *et al.*, *Angew. Chem. Int. Ed.*, 2015, **54**, 1336.

O 45.11 Tue 18:30 P1A

**Topology Dependent Molecule-Substrate Interactions: Azulene vs. Naphthalene in Temperature-Programmed Desorption** — ●STEFAN RENATO KACHEL, MAIK SCHÖNIGER, MARTIN SCHMID, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Germany

Understanding the interaction of  $\pi$ -conjugated organic molecules with metal surfaces is crucial for the development of modern organic electronic devices. To uncover how the topology of the  $\pi$ -system influences the surface chemical bond, the structural isomers azulene and naphthalene on Ag(111) and Cu(111) were investigated by temperature-programmed desorption. While naphthalene has a benzoid, alternant topology, azulene is a prototypical example for a  $\pi$ -system with a non-alternant topology. On Cu(111), azulene has a much higher desorption temperature (520 K) than naphthalene (340 K) in the limit of low coverage, while the difference is less pronounced on Ag(111). With increasing submonolayer coverage, all systems show substantial peak broadening towards lower temperatures, which is typical for intermolecular repulsion. The effect is most pronounced for azulene/Cu(111), where the monolayer signals spread over almost 300 K. Refined analysis on the basis of heating-rate variation studies provides desorption energies of 165 kJ/mol for azulene and 100 kJ/mol for naphthalene, both on Cu(111). The large energy difference indicates that the topology of the molecular  $\pi$ -system has enormous influence on the molecule-substrate interaction.

O 45.12 Tue 18:30 P1A

**Topologically Different Aromatic Isomers on Metal Surfaces: A Molecular Model System for 5-7 Defects in Graphene** — ●KATHARINA K. GREULICH<sup>1</sup>, BENEDIKT P. KLEIN<sup>1</sup>, NADINE VAN DER HEIJDEN<sup>1</sup>, CLAUDIO K. KRUG<sup>2</sup>, STEFAN R. KACHEL<sup>1</sup>, MAIK SCHÖNIGER<sup>1</sup>, PHIL ROSENOW<sup>1</sup>, MARTIN SCHMID<sup>1</sup>, RALF TONNER<sup>1</sup>, INGMAR SWART<sup>2</sup>, and J. MICHAEL GOTTFRIED<sup>1</sup> — <sup>1</sup>Fachbereich Chemie, Philipps-Universität Marburg, Germany — <sup>2</sup>Debye Institute for Nanomaterial Science, Utrecht University, The Netherlands

While conjugated systems with alternant topologies and their interaction with metal surfaces have been subject to intensive investigation, much less is known about their non-alternant isomers. A conjugated system with non-alternant topology occurs in the 5-7 defects of graphene. As a molecular model system for these defects, we investigated azulene and compared it to naphthalene as a model for the regular 6-6 motif. Both molecules were studied on Cu(111) and Ag(111) surfaces with PES, NEXAFS, TPD, nc-AFM, STM and periodic DFT calculations. The non-alternant topology causes non-uniform charge distribution and more localized frontier orbitals, resulting in a much stronger and more localized interaction with both metal surfaces. Manifestations of the stronger interaction of the non-alternant molecule with the surface include interfacial charge transfer and substantial in-plane and out-of-plane deformations. The latter result from the donation of electron density into the LUMO of the non-alternant molecule.

O 45.13 Tue 18:30 P1A

**Effects of Surface Modification by Silane Based Self-Assembled Monolayers** — ●FRANZISKA MAERCKS, JULIA RITICH,

SEBASTIAN JUNG, CAROLIN C. JACOBI, and MATTHIAS WUTTIG — I. Institute of Physics (IA), RWTH Aachen University, Germany

The performance of organic devices such as Organic Light Emitting Diodes (OLED) or Organic Thin Film Transistors (OTFT) depends on the interfaces between the different layers. Hence, the optoelectronic device properties can be strongly altered by the choice of electrode material. Therefore, it is important to investigate the organic-inorganic interface with respect to electronic structure changes driven by electrode surface functionalization.

A unique class of modifications is provided by Self-Assembled Monolayers (SAMs). This type of modification is able to tailor the work function of the electrode. Furthermore, the growth of a subsequently deposited organic layer can be influenced. In this study silicon (001) substrates were modified by silane based SAMs. The work function change and the electronic structure at the interface is investigated with photoelectron spectroscopy measurements (XPS, UPS, IPES) allowing us to investigate the interaction of the organic layer and the SAM modified electrode surface.

O 45.14 Tue 18:30 P1A

**The initial stages and local configurations of ultrathin TiOPc layers on Ag(111)** — ●SEBASTIAN THUSSING, LAURA FERNANDEZ, ALEXANDER MÄNZ, GREGOR WITTE, and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, 35032 Marburg, Germany

The evolution of titanyl-phthalocyanine (TiOPc) thin films grown on Ag(111) has been investigated using IRAS, SPA-LEED, TDS and STM. In the (sub)monolayer regime a 2D-gas, a commensurate (*c*) and a point-on-line (POL) phase can be observed, thereby the non-planar TiOPc molecule is adsorbed in an oxygen-up configuration with the molecular backbone oriented parallel to the surface. The *c*-phase contains two molecules at inequivalent adsorption sites within the unit cell displaying different azimuthal orientations with respect to the Ag(111) substrate. Approaching full saturation (POL-phase) Pauli repulsion leads to a further azimuthal reorientation that enables a higher packing density. By monitoring the prominent Ti=O stretching mode in IRAS and identifying local molecular packing configurations in STM, a microscopic model for the growth of TiOPc bilayers on Ag(111) is suggested and defect structures within these bilayers are identified. The TiOPc bilayer displays a high thermal stability up to 500 K, which is attributed to hydrogen bonds between oxygen of the titanyl unit and the hydrogen rim of phthalocyanines in the second layer, in addition to contributions arising from the oppositely oriented axial dipole moments and the ubiquitous van der Waals interactions.

O 45.15 Tue 18:30 P1A

**Morphology and Electronic Structure of Tris-HCl crystals on pure and alloyed gold surfaces** — ●SEYMA NAYIR and OĞUZHAN GÜRLÜ — Istanbul Technical University, Department of Physics, Maslak, 34469, Istanbul, Turkey

Tris-HCl is one of the components of widely used buffer solution Tris-EDTA for the storage of DNA and RNA. Apart from the biological studies and medicine, tris also finds use in solar cell systems as an organic thermal energy storage material. When drop casted from the solution, Tris-HCl crystallizes on gold coated pure mica and gold coated chromium on mica surfaces differently. In this work we investigated the reasons for differences in such crystallization behavior of Tris-HCl. The surface topography and crystalline structure of Tris-HCl deposits were investigated by atomic force microscopy. Additionally we performed Kelvin Probe Force Microscopy measurements in order to measure the local contact potential difference of Tris-HCl crystallites and films on gold surfaces, and calculated the local work function changes. Our results indicate a strong dependence of the crystallization behavior of the Tris-HCl on the electro-static landscape of the host surfaces rather than their morphology.

O 45.16 Tue 18:30 P1A

**Light-induced spin-state switching in Fe(II) spin-crossover thin films on TiTe<sub>2</sub> studied with NEXAFS and ARPES** — ●SIMON JARAUSCH<sup>1</sup>, SEBASTIAN ROHLF<sup>1</sup>, MATTHIAS KALLÄNE<sup>1</sup>, BENEDIKT FLÖSER<sup>2</sup>, FELIX TUCZEK<sup>2</sup>, and KAI ROSSNAGEL<sup>1</sup> — <sup>1</sup>Institut für Experimentelle und Angewandte Physik, Universität Kiel, 24098 Kiel, Germany — <sup>2</sup>Institut für Anorganische Chemie, Universität Kiel, 24098 Kiel, Germany

Coordinative Fe(II) complexes are model systems for organic molecules whose electronic, magnetic, and structural properties can be manipulated by external stimuli. Moreover, the temperature- and light-driven

spin transitions observed in a number of these materials may provide a suitable testbed for the development of future spintronic devices. The temperature- and light-induced spin-state switching of the spin-crossover complex (SCO) Fe(H<sub>2</sub>bpz)<sub>2</sub>(phen) adsorbed on Au(111) is well established, but not preserved for molecules in direct contact to the surface due to molecular dissociation. To avoid this effect, one can either increase the stability of the SCO complex or reduce the substrate-mediated interactions. For the latter approach, the layered transition-metal dichalcogenide TiTe<sub>2</sub> may be a promising alternative due to its weak van-der-Waals-like interaction with adsorbates. Here, we present a combined near edge X-ray absorption fine structure (NEXAFS) spectroscopy and angle-resolved photoemission spectroscopy (ARPES) study of the spin-state switching of a stabilized Fe(H<sub>2</sub>bpz)<sub>2</sub>(phen) derivative adsorbed on TiTe<sub>2</sub>.

O 45.17 Tue 18:30 P1A

**On-Surface Synthesis of Naphthalocyanine and Corrole Complexes** — ●MALTE ZUGERMEIER<sup>1</sup>, MIN CHEN<sup>1</sup>, LUKAS HEUPLICK<sup>1</sup>, MARTIN LIEBOLD<sup>1</sup>, NICOLAS BOCK<sup>1</sup>, FALK NIEFIND<sup>1</sup>, LUKAS RUPPENTHAL<sup>1</sup>, MARTIN SCHMID<sup>1</sup>, PETER SCHWEYEN<sup>2</sup>, MARTIN BRÖRING<sup>2</sup>, JÖRG SUNDERMEYER<sup>1</sup>, and J. MICHAEL GOTTFRIED<sup>1</sup> — <sup>1</sup>Fachbereich Chemie, Philipps-Universität Marburg, Germany — <sup>2</sup>Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Germany

Tetrapyrrole macrocycles are important examples of biomimetic systems that found the way into real-life applications. Porphyrins possess interesting catalytic and optoelectronic properties. The usage of their metal complexes for surface functionalization can benefit from oxidation state tuning of the metal center to control its chemical and electronic properties. This is possible with axial ligands or modifications of the equatorial tetrapyrrole ligand. In contrast to porphyrins, adsorbed corroles can oxidize metal atoms to their +III oxidation state. For detailed insight into this surface coordination reaction, we studied mono- and multilayers of an octa-alkyl corrole and their reaction with transition metals by XPS, UPS, NEXAFS and STM. Furthermore, we report the on-surface synthesis of the closely related porphyrins and corroles related, artificial naphthalocyanines on Ag(111) by tetramerization of dicyanonitriles in the presence of iron. STM and XPS studies reveal that pre-reaction dicyanonitrile forms organometallic structures with the Fe atoms, whereas the post-reaction layer consists of iron naphthalocyanine complexes.

O 45.18 Tue 18:30 P1A

**Surface crystallography of large organic molecules on metal and insulator surfaces by LEED-IV using Fourier coefficients** — ●INA KRIEGER<sup>1,3</sup>, GEORG HELD<sup>2</sup>, CHRISTIAN KUMPF<sup>3</sup>, and MORITZ SOKOLOWSKI<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Bonn, 53115 Bonn, Germany — <sup>2</sup>Department of Chemistry, University of Reading and Diamond Light Source, UK — <sup>3</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52428 Jülich, Germany

We will report on LEED-IV analysis of the large organic molecules PTCDA and NTCDA on the metal and insulator surfaces Ag(100), Ag(111), and KCl(100). Using data from different angles of electron incidence and optimizing the LEED-IV program code we were able to extend the experimental data set and shorten the calculation times required for the complex and large unit cells. Furthermore, the distortion of the PTCDA molecule and the buckling of the Ag surface were described by Fourier coefficients taking into account the symmetry of the system [1]. The idea of this procedure is to suppress unphysical vertical displacements of atoms on a short-wave-length scale by restriction to lower order coefficients.

By this, we obtain good Pendry R-factors, for PTCDA/Ag100 of about 0.23. We were able to derive the vertical distortions of the oxygen atoms in the functional group and the buckling of the Ag surface in rather good agreement with earlier results from DFT and NIXSW studies.

[1] W. Moritz et al, Phys. Rev. Lett. 104, 136102 (2010).

O 45.19 Tue 18:30 P1A

**Theoretical Insights into Highly Selective Organic-Inorganic hybrid NO<sub>2</sub> Gas Sensors** — ●GIULIO COCCO<sup>1</sup>, LEONHARD MAYRHOFER<sup>1</sup>, ALAAELDIN GAD<sup>2</sup>, OLGA CASALS<sup>3</sup>, NICOLAI MARKIEWICZ<sup>2</sup>, JUAN PRADES<sup>3</sup>, ANDREAS WAAG<sup>2</sup>, and MICHAEL MOSELER<sup>1</sup> — <sup>1</sup>Freiburg Materials Research Center, University of Freiburg, D-79104 Freiburg, Germany — <sup>2</sup>Institute for Semiconductor Technology, Braunschweig University of Technology, Hans-Sommer-

Straße 66, D-38106 Braunschweig, Germany — <sup>3</sup>MIND-IN<sup>2</sup>UB, Department of Electronics, University of Barcelona, C/Martí i Franquès 1, E-08028 Barcelona, Spain

The low selectivity of inorganic gas sensors is among the issues hindering their applications in environmental monitoring. Semiconductor nanowires (NWs) functionalized by self-assembled monolayers (SAMs) of organic molecules are a promising class of materials offering selectivity and sensitivity towards single gas species [1][2][3]. DFT simulations will be used to give insights on this new approach of highly selective NO<sub>2</sub> gas sensors. However, moisture is a critical factor influencing stability and responses towards gas. A novel concept of mixed SAMs is introduced to improve such issues. Here, by means of DFT, we analyze the different responses of NWs functionalized with silanes toward NO<sub>2</sub> at different relative humidity. We show that water can modify the response although no direct electronic interaction between water and functionalized NWs is observed.

[1]Adv. Funct. Mater. **2014**,24, 595 [2]Adv. Mater.**2014**, 26, 8017 [3]ACS Sensors **2016**, accensors.6b00508

O 45.20 Tue 18:30 P1A

**Deposition of tetracene on Si(111)-(7x7)** — ●CHRISTIAN VÖLKNER, BAHAAEDDIN IRZIQAT, KEVIN OLDENBURG, INGO BARKE, and SYLVIA SPELLER — University of Rostock, Institute of Physics, 18059 Rostock, Germany

Organic electronics and their individual components are becoming increasingly smaller nowadays. To precisely control the deposition of small amounts of organic molecules on a substrate a dedicated evaporator chamber was built and attached to a commercial Low Temperature Scanning Tunneling Microscope system. The performance of the evaporator is evaluated depositing tetracene molecules on Si(111)-(7x7). The structure of the tetracene layers is investigated.

O 45.21 Tue 18:30 P1A

**Vibrational properties of organic thin films on graphene/Ru(0001)** — ●SEBASTIAN FLADE and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, 35032 Marburg, Germany

Ultrathin films of fullerene (C<sub>60</sub>) and pentacene (PEN) have been prepared on graphene/Ru(0001) and their vibrational properties, as well as thermal evolution investigated by using Fourier-transform infrared spectroscopy. Monolayer species are found to display distinctly different vibrational signatures as compared to higher layers which indicates a weak chemical interaction. From the variation of relative intensities of vibrational modes structural changes within the organic films are derived. In particular, the thermal stability of grown layers, as well as their layered structure in case of C<sub>60</sub> - PEN heterolayers on g/Ru(0001) has been monitored. Comparison to layers deposited directly on the Ru(0001) surface illustrates the effect of graphene acting as a passivation layer between the transition metal substrate and the molecular film.

O 45.22 Tue 18:30 P1A

**Polarization-Dependent Excitation of Porphyrin Nanostructures investigated by PEEM** — HANNES HARTMANN, KARL-HEINZ MEIWES-BROER, ●INGO BARKE, and SYLVIA SPELLER — University of Rostock, Institute of Physics, 18059 Rostock

In photoemission the dependence on light polarization can help to access the internal structure of molecule aggregates. Recently we selectively mapped excited states in copper tetraundecylporphyrin (CuTUP) nanostructures on graphite (HOPG) using two-photon photoemission electron microscopy (2PPE-PEEM) [1]. Here we present polarization-dependent and spatially resolved electron yields of the same system using varying excitation wavelengths. We observe a Davydov-like splitting of the Soret band which shows a systematic dependence on the specific location. By varying the light polarization this spatial effect is correlated with the direction of the transition dipole moments. These results are discussed in view of orientation and internal structure of the CuTUP assemblies. In addition we observe characteristic variations of the photoelectron intensity which is found to be connected to the local height as determined by correlative atomic force microscopy measurements. This behavior is analyzed in the framework of vertical optical standing waves within the CuTUP structures.

[1] H. Hartmann et al., J. Phys. Chem. C **120**, 16977 (2016)

O 45.23 Tue 18:30 P1A

**The Ionic Liquid|Graphite(0001) and Ionic Liquid|Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>(111) Interface as a Model for the Electrode|Electrolyte interface in Li-ion Batteries** — ●JIHYUN KIM<sup>1</sup>, FLORIAN BUCHNER<sup>2</sup>, CHRISTIANE ADLER<sup>1</sup>, MARAL BOZORGCHENANI<sup>1</sup>, JOACHIM BANSMANN<sup>1</sup>, and R. JÜRGEN BEHM<sup>1,2</sup> — <sup>1</sup>Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — <sup>2</sup>Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, D-89081 Ulm, Germany

In this ultrahigh vacuum model study, we explore two anode processes which are highly important for the function of Li-ion batteries: (1) the reversible inter- and deintercalation of lithium (Li) and (2) the formation of the so-called electrode|electrolyte interface (EEI). Employing X-ray and UV photoelectron spectroscopy (XPS / UPS) and using well-defined anode surfaces such as graphite (0001) and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (111) (LTO) we found that vapor deposition of metallic Li on graphite (0001) at 80 K results in partially charged Li<sup>δ+</sup> atoms, while for deposition at 300 K Li intercalates, forming Li<sub>x</sub>C<sub>6</sub>. Using Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as substrate, Li diffuses into the bulk for deposition at 300 K as well, while for deposition at 80 K XPS reveals the formation of very small amounts of Ti<sup>3+</sup>. Evidently, under these conditions some of the Li remains near the surface, generating the Li-rich Li<sub>7</sub>Ti<sub>5</sub>O<sub>12</sub> phase, while the majority dissolves into the bulk. Finally, to mimic the EEI, we studied the temperature-dependent interaction of (sub-)monolayers of the ionic liquid [BMP][TFSA] with both graphite/lithiated graphite and the Li-poor/Li-rich LTO.

O 45.24 Tue 18:30 P1A

**Spectroscopy from 1,3-Diphenylisobenzofuran films on Cu(111) and Au(100)** — ●JANEK RIEGER, ANGELIKA DEMLING, DAVID NOBIS, DANIEL NIESNER, FEIFEI XIANG, M. ALEXANDER SCHNEIDER, and THOMAS FAUSTER — Lehrstuhl für Festkörperphysik, FAU Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen, Germany

Thin films of 1,3-Diphenylisobenzofuran (DPIBF) show singlet fission, a mechanism for multi-exciton generation that might be used to enhance the efficiency of organic photovoltaics [1]. The yield of singlet fission depends strongly on the structural polymorph of the film [2]. Mixtures of several polymorphs were shown to form on oxide substrates. We use optical and photoelectron spectroscopies, scanning tunneling microscopy and thermal desorption spectroscopy to investigate DPIBF deposited on Cu(111) and Au(100) by thermal evaporation. Results are presented for various growth temperatures and for film thicknesses from one monolayer to 40 nm. While growth on Au(100) results in coexisting structures at all tested conditions, phase-pure films are prepared on Cu(111). The first layer adsorbs in an ordered structure at room temperature, with a molecular arrangement similar to the one in crystals. For thicker films, single series of photoluminescence peaks are found. The singlet transition blueshifts with increasing preparation temperature for DPIBF on both substrates. The maximum singlet energy is close to 2.8 eV, sufficient to support singlet fission [2].

[1] J. C. Johnson et al., J. Am. Chem. Soc. **132** (2010) 16302

[2] J. L. Ryerson et al., J. Phys. Chem. C **118** (2014) 12121

O 45.25 Tue 18:30 P1A

**Dielectric properties of carbon nanomembranes prepared from aromatic self-assembled monolayers investigated by impedance spectroscopy** — PAUL PENNER, EMANUEL MARSCHEWSKI, ●XIANGHUI ZHANG, and ARMIN GÖLZHÄUSER — Faculty of Physics, University of Bielefeld, 33615 Bielefeld

Carbon nanomembranes (CNMs) are two-dimensional materials that are made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Here we investigate the dielectric properties of pristine SAMs and CNMs with an EGaIn top electrode by impedance spectroscopy. Analysis and comparison of the tunneling resistance and capacitance density of pristine and cross-linked SAMs revealed a thickness dependent capacitance associated with the monolayer as well as a thickness independent capacitance. The latter could be attributed to the appearance of a new interface due to the decoupling of molecules from the underlying gold surface upon electron irradiation. We adopted an equivalent circuit to take into account the interfacial capacitance as well as the oxide layer of the EGaIn top electrode. An interfacial capacitance of about 5 fF/μm<sup>2</sup> was obtained for CNM-based molecular junctions. The tunneling decay constant β remains unaffected after electron irradiation, which exhibits a value of about 0.5 Å<sup>-1</sup> for both systems. Determination of dielectric constants of SAMs and CNMs from the impedance spectra will also be analyzed and discussed.

O 45.26 Tue 18:30 P1A  
**Investigating the orientation of halogenated benzene molecules on Cu(111) surfaces using IR spectroscopy**  
— •CHRISTINA PENTZEK and KARINA MORGENSTERN — Ruhr-Universität Bochum, Chair of Physical Chemistry I, Germany

Adsorption of organic molecules on metal surfaces is important to understand the mechanisms in heterogeneous catalysis. In this study, vibrational spectra of chlorobenzene and bromobenzene molecules adsorbed on a Cu(111) surface are investigated by reflection-absorption

infrared spectroscopy (RAIRS). While it is well established that unsubstituted benzene molecules adsorb with their molecular plane in parallel to the surface, it is not known how halogen molecules influence the adsorption orientation. Because of the selection rules of RAIRS we are able to identify the orientation of halogenated benzene molecules on Cu(111) surfaces. However, the vibration modes depend on the layer thickness of molecules at the surface. In this presentation we want to discuss different orientations of halogenated benzenes at different coverages at low temperatures.