

## O 38: Organic Molecules on Inorganic Substrates II: Electronic Properties and Charge Transfer

Time: Tuesday 14:00–16:45

Location: H24

O 38.1 Tue 14:00 H24

**Electronic properties of NiOEP on copper: a molecular orbital tomography study** — ●H. STURMEIT<sup>1</sup>, G. ZAMBORLINI<sup>1</sup>, S. PONZONI<sup>1</sup>, M. JUGOVAC<sup>2</sup>, V. FEYER<sup>2</sup>, C. M. SCHNEIDER<sup>2</sup>, and M. CINCHETTI<sup>1</sup> — <sup>1</sup>TU Dortmund, 44227 Dortmund, Germany — <sup>2</sup>Forschungszentrum Jülich, 52428 Jülich, Germany

$\pi$ -conjugated organic molecules are considered a valuable alternative to inorganic semiconductors as their electronic, optical and magnetic properties can be tailored at the atomic level. Supporting organic films with metal substrates within an organic-based device, may lead to chemical reactions, hybridization, and/or charge transfer at the metal/organic interface, ultimately affecting the device performance. Recently, this has been shown for nickel tetraphenylporphyrin (NiTPP) evaporated on Cu(100), whose frontier orbitals get partially filled up to the LUMO+3 [Zamborlini et al, Nat. Comm. 8, 335, 2017] due to a consistent charge transfer at the interface. In the present work, we studied the impact of the peripheral substituents of the porphyrin macrocycle on the charge transfer. To achieve this goal, nickel octaethylporphyrin (NiOEP) molecules, where the four phenyl ligands are replaced with eight ethyl terminations in the  $\beta$ -positions of the pyrrole moieties, were sublimated on the (100) copper surface. The overall energy level alignment at the metal/organic interface was characterized by means of molecular orbital tomography. Our preliminary measurements show that changing the periphery does not strongly influence the overall charge transfer: the LUMO+3 remains partially filled while shifting its energetic position by a few tens of meVs.

O 38.2 Tue 14:15 H24

**Molecular Orbital Imaging Beyond the First Monolayer** — ●CHRISTIAN METZGER<sup>1</sup>, MANUEL GRIMM<sup>1</sup>, MARTIN GRAUS<sup>1</sup>, KIANA BAUMGÄRTNER<sup>1</sup>, MATTEO JUGOVAC<sup>2</sup>, GIOVANNI ZAMBORLINI<sup>2</sup>, VITALIY FEYER<sup>2</sup>, ACHIM SCHÖLL<sup>1</sup>, and FRIEDRICH REINERT<sup>1</sup> — <sup>1</sup>Julius-Maximilians-Universität Würzburg, Experimental Physics VII, 97074 Würzburg, Germany — <sup>2</sup>Forschungszentrum Jülich GmbH, Paul Grünberg Institute (PGI-6), 52425 Jülich, Germany

We present a method to determine the geometric alignment of molecular compounds within evaporated thin films by a combination of experimental orbital imaging combined with photoemission matrix element calculations on the example of pentacene bilayers on Ag(110). The technique utilizes angle-resolved photoemission spectroscopy (ARPES) measurements at a photoemission electron microscope in Fourier-space imaging mode (kPEEM), which enables the efficient detection of photoelectrons emitted into the entire hemisphere above the sample. By simulating different tilt angles of isolated pentacene molecules and comparing the resulting photoemission intensity distribution with momentum maps measured on molecular multilayers, one is able to determine the molecules' tilt angles for each separate layer independently from one another. We determine that the flat-lying molecules of the first monolayer on the metal substrate exhibit a noticeable tilt angle upon adsorption of a second molecular layer. The molecules in the second layer above the substrate feature a larger inclination, which is evidence of the gradual relaxation into the pentacene bulk structure with increasing film thickness.

O 38.3 Tue 14:30 H24

**Strong and weak interactions of metal organic networks with metal surface: adsorption geometry and electronic structure.** — ●IULIA COJOCARIU<sup>1</sup>, MATTEO JUGOVAC<sup>1</sup>, GIOVANNI ZAMBORLINI<sup>2</sup>, VITALIY FEYER<sup>1</sup>, and CLAUDIU M. SCHNEIDER<sup>2,3</sup> — <sup>1</sup>PGI-6, Forschungszentrum Jülich GmbH, Germany — <sup>2</sup>TU Dortmund, Exp. Phys. VI, Germany — <sup>3</sup>Fakultät für Physik and CENIDE, Universität Duisburg-Essen, Germany

We report a study of the adsorption behaviour of iron phthalocyanine (FePC) in the first and second layer atop of low-index crystal faces of silver. The combination of low-energy electron diffraction and molecular orbital tomography (MOT) allows the determination of the superstructure unit cell and the azimuthal orientation of the molecules with respect to the substrate. Additionally, momentum patterns give information about the electronic structure and the symmetry of molecular orbitals in the first and second organic layer.

Within the MOT approach, it is possible to disentangle the contribution of the first and the second FePC long-range ordered layers

to the whole valence band spectrum. While the first exhibit strong hybridization and charge transfer with the metal surface (as pointed by partially filled LUMOs in the momentum maps), the second is decoupled. This analysis allows us to understand the peculiarities of the phenomena at the organic/metal interface.

Experiments were carried out at the NanoESCA beamline at Elettra. The setup includes a PEEM that directly images parallel momentum component ( $k_x, k_y$ ) of emitted photoelectrons at a fixed binding energy.

O 38.4 Tue 14:45 H24

**Spin- and angle-resolved photoemission study of heteromolecular bilayer films on ferromagnets** — ●BENITO ARNOLDI<sup>1</sup>, STEFAN LACH<sup>1</sup>, ROBERT RANECKI<sup>1</sup>, JOHANNES STÖCKL<sup>1</sup>, MIRKO CINCHETTI<sup>2</sup>, BENJAMIN STADTMÜLLER<sup>1</sup>, CHRISTIANE ZIEGLER<sup>1</sup>, and MARTIN AESCHLIMANN<sup>1</sup> — <sup>1</sup>Department of Physics, University of Kaiserslautern, Erwin-Schrodinger-Strasse 46, 67663 Kaiserslautern, Germany — <sup>2</sup>Experimentelle Physik VI, Technische Universität Dortmund, Otto-Hahn-Str. 4, 44221 Dortmund, Germany

Heteromolecular bilayer films on ferromagnetic surfaces are highly intriguing molecular assemblies to study and control the spin-dependent electronic properties of these so called spinterfaces. In these systems, the first molecular layer is strongly hybridized with the surface while the molecular character of the second layer molecules is largely preserved.

Here, we focus on such a heteromolecular bilayer film consisting of C60 grown on the CuPc/Co(001) interface. The spin dependent electronic structure of this adsorbate system is investigated by spin- and angle resolved photoemission. Using a dedicated data analysis scheme, we are able to distinguish the formation of hybrid interface states at the CuPc/Co interface as well as charge transfer induced interface states at the heteromolecular interfaces from elastic scattering effects of photoelectrons in the molecular stack. Our results will be discussed in the light of local scanning tunnel spectroscopy data recorded for the same material system. This allows a direct assignment of spectroscopic signals to the different parts of the heteromolecular bilayer film.

O 38.5 Tue 15:00 H24

**Electronic decoupling of PTCDA by a single layer of hexagonal boron nitride on Cu(111)** — ●CHRISTINE BRÜLKE<sup>1</sup>, TIMO HEEPENSTRICK<sup>1</sup>, INA KRIEGER<sup>1</sup>, BEATRICE WOLFF<sup>1</sup>, XI-AOSHENG YANG<sup>2</sup>, ALI SHAMSADDINLOU<sup>2</sup>, SIMON WEISS<sup>2</sup>, FRANCOIS C. BOCQUET<sup>2</sup>, F. STEFAN TAUTZ<sup>2</sup>, SERGUEI SOUBATCH<sup>2</sup>, and MORITZ SOKOLOWSKI<sup>1</sup> — <sup>1</sup>Universität Bonn, Institut für Physikalische und Theoretische Chemie, 53115 Bonn, Germany — <sup>2</sup>Forschungszentrum Jülich, Peter Grünberg Institut (PGI-3), 52425 Jülich, Germany

Hexagonal boron nitride (hBN) has previously been investigated regarding its function as a template for organic molecules as well as its ability to decouple them from an underlying metal substrate. We report on the ability of hBN to decouple the model molecule PTCDA from a Cu(111) substrate using structural and spectroscopic methods and present quantitative data that characterize the adsorption complex. SPA-LEED and STM investigations show that the lateral structure of the monolayer conforms to the (102) planes of the bulk configurations within less than 4%. NIXSW experiments reveal that the molecules are positioned at a large distance of 3.38 Å above the surface with a very small distortion out of the molecular plane by only 2.6%. Furthermore, photoelectron spectroscopy (XPS, UPS) shows that there is no hybridization of molecular and metal states. All of these features differ significantly from those found for PTCDA on metal surfaces. The electronic decoupling of the PTCDA molecule from the metal substrate is further proven by the non-vanishing fluorescence yield of the monolayer because otherwise mixing of electronic states leads to quenching.

O 38.6 Tue 15:15 H24

**Using self-assembled monolayers for controlling charge-carrier injection into organic transistors** — ANDREAS PETRITZ<sup>1</sup>, MARKUS KRAMMER<sup>2</sup>, ERIC SAUTER<sup>3</sup>, MICHAEL GÄRTNER<sup>4</sup>, GIULIA NASCIMBENI<sup>2</sup>, ANDREEA COJOCARU<sup>1</sup>, ESTHER KARNER-PETRITZ<sup>1</sup>, ROLAND RESEL<sup>2</sup>, ANDREAS TERFORT<sup>4</sup>, MICHAEL ZHARNIKOV<sup>3</sup>, KARIN ZOJER<sup>2</sup>, BARBARA STADLOBER<sup>1</sup>, and ●EGBERT ZOJER<sup>2</sup> — <sup>1</sup>Joanneum Research, MATERIALS-Institute for Surface Technologies and Photonics, Austria — <sup>2</sup>Institute of Solid State Physics, Graz Uni-

versity of Technology, Austria — <sup>3</sup>Applied Physical Chemistry, Heidelberg University, Germany — <sup>4</sup>Institut für Anorganische und Analytische Chemie, Goethe-University Frankfurt, Germany

We show how self-assembled monolayers (SAMs) bearing embedded polar groups can be used for tuning contact resistances in organic thin-film transistors by three orders of magnitude.[1] The chosen approach also allows the realization of flexible p- and n-type transistors using Au electrodes.[1] An in-depth surface science investigation of the SAMs and the organic layers grown on top of them [1,2,3] show that the tunability of the contact resistance is a consequence of SAM-induced work function changes. Additionally, the dependence of tunneling transport through the SAMs on their chemical structure plays an important role.[1,4] The experimental results are rationalized by density-functional theory calculations. [1] A. Petritz et al., *Adv. Funct. Mater.*, 1804462 (2018). [2] M. Gärtner et al., *J. Phys. Chem. C*, published on-line [3] T. Abu-Husein et al., *Adv. Funct. Mater.* 25, 3943 (2015). [4] A. Kovalchuk et al., *Chem. Sci.* 7, 781 (2016)

O 38.7 Tue 15:30 H24

**Reliable Modeling of the Charge Transfer Mechanism at Inorganic/Organic Interfaces** — ●ELISABETH WRUSS, EGBERT ZOJER, and OLIVER T. HOFMANN — Institute of Solid State Physics, Graz University of Technology, Graz, Austria

Charge transfer between substrate and adsorbate is one of the determining factors for the electronic structure at inorganic/organic interfaces. In this work we raise the question how well this property can be simulated using DFT and how the results are influenced by the chosen methodology as well as by assumptions regarding the interface structure. We focus on hybrid functionals, elucidating the interplay between the charge transfer mechanism (integer vs. fractional charge transfer) and the applied amount of Hartee-Fock-like exchange. As an exemplary system, we use tetrafluoro-1,4-benzoquinone adsorbed on Cu and Cu<sub>2</sub>O. We find that the simulated charge transfer mechanism is determined by a delicate interplay of the DFT functional and the physical properties of the system, such as hybridization strength, the size of the adsorbed molecule, and the surface polarizability. As a next step, we go beyond the simplified idea of perfect metallic or insulating substrates and include surface defects. By acting as reaction centers, such defects strongly impact the interaction between substrate and adsorbate and lead to charge transfer even in situations in which this would not be expected for idealized systems. Our results highlight that not only a proper choice of the DFT functional, but also the consideration of realistic, defect-afflicted surfaces is crucial for reliably modeling charge transfer at interfaces.

O 38.8 Tue 15:45 H24

**Modifying the tunneling decay coefficients of self-assembled monolayer junctions** — XIAOPING CHEN<sup>1</sup>, HARSHINI ANNADATA<sup>1</sup>, ●BERNHARD KRETZ<sup>2</sup>, DAVID ALEXANDER EGGER<sup>2</sup>, and CHRISTIAN NIJHUIS<sup>1,3,4</sup> — <sup>1</sup>Department of Chemistry, National University of Singapore, Singapore — <sup>2</sup>Institute of Theoretical Physics, University of Regensburg, Regensburg, Germany — <sup>3</sup>Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore — <sup>4</sup>NUSNNI-Nanocore, National University of Singapore, Singapore

The development and improvement of molecular electronic devices requires insight into charge transport across organic-inorganic interfaces. Charge transfer rates in the quantum tunneling transport regime strongly depend on the tunneling decay coefficient  $\beta$ , which determines the decline of the current across the junction as a function of the length and the barrier height. It is well-known that the value of  $\beta$  of self-assembled monolayer (SAM) junctions depends on the specific electronic structure of the molecular backbone. Combining experiments and computer simulations, we demonstrate that  $\beta$  of a non-conjugated SAM junction can be altered by using different halogens as termination on one side of the molecular backbone. Our experiments indicate that this modification of the tunneling coefficient is correlated with a change in the dielectric constant. Furthermore, our calculations shed some light on how the frontier orbitals and transmission channels are affected by the change of the end-group.

O 38.9 Tue 16:00 H24

**Charge distribution within molecular dipoles and their influence on the local work function of the substrate** — ●SERGEY TRISHIN<sup>1</sup>, DANIELA ROLF<sup>1</sup>, CHRISTIAN LOTZE<sup>1</sup>, PHILIPP RIETSCH<sup>2</sup>,

SIEGFRIED EIGLER<sup>2</sup>, and KATHARINA J. FRANKE<sup>1</sup> — <sup>1</sup>Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany — <sup>2</sup>Institut für Chemie und Biochemie, Freie Universität Berlin, 14195 Berlin, Germany

Donor-acceptor (DA) molecules exhibit two charge-separated moieties, which makes them interesting for application in molecular electronics. However, deposition on metal surfaces, which may be necessary for certain applications, can alter the charge distribution of DA molecules due to screening and hybridization effects.

We study Ethyl-Diaminodicyanoquinone molecules on a Au(111) surface with scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (nc-AFM). By mapping the local contact potential difference (LCPD) over the molecules we show that the intrinsic dipole moment of the molecules is partially preserved upon adsorption on the Au(111) surface. Moreover the molecular orbitals appear to be shifting across the molecule. This shift follows the variation of the LCPD signal. Both findings can be explained by vacuum-pinned energy levels and local changes in the work function due to the molecular charges. An overall reduction of the work function is related to a local scale push-back effect. There molecules push back substrate electrons, which are leaking out into the vacuum.

O 38.10 Tue 16:15 H24

**Mixed monomolecular films with embedded dipolar groups on Ag(111)** — ERIC SAUTER<sup>1</sup>, CHARLES-OLIVIER GILBERT<sup>2</sup>, JEAN-FRANÇOIS MORIN<sup>2</sup>, ANDREAS TERFORT<sup>3</sup>, and ●MICHAEL ZHARNIKOV<sup>1</sup> — <sup>1</sup>Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — <sup>2</sup>Département de Chimie and Centre de Recherche sur les Matériaux Avancés, Université Laval, Québec, Canada G1V 0A6 — <sup>3</sup>Institut für Anorganische und Analytische Chemie, Universität Frankfurt, 60438 Frankfurt, Germany

We studied the application of the concept of embedded dipole in monomolecular self-assembly to the Ag(111) substrate, using two different types of molecules with either pyrimidine groups embedded into aromatic backbones or ester groups embedded into aliphatic backbones as test systems. The orientation of the embedded group was varied and the molecules with the oppositely oriented dipoles were combined together as mixed self-assembled monolayers (SAMs). Pronounced electrostatic effects of the dipolar groups were observed, reflected, in a consistent manner, by the electrostatic shift in photoemission and by work function variation. The character and extent of these effects could be explained in context of molecular orientation. The pyrimidine-substituted SAMs were found to be especially useful for the electrostatic interface engineering, allowing, in the case of Ag, a flexible tuning of the work function in the ca. 0.85 eV range without changing the character of the SAM-substrate and SAM-ambient interfaces. An analogous behavior can also be expected for other substrates.

O 38.11 Tue 16:30 H24

**Understanding the interplay of chemical and electrostatic effects for the core level spectra characterizing metal-organic interfaces** — ●GIULIA NASCIMBENI<sup>1</sup>, MICHAEL ZHARNIKOV<sup>2</sup>, and EGBERT ZOJER<sup>1</sup> — <sup>1</sup>Institute of Solid State Physics, Graz University of Technology, Austria — <sup>2</sup>Applied Physical Chemistry, Heidelberg University, Germany

Polar organic monolayers (POMs) are widely used in the field of organic electronics to manipulate the work function of metallic electrodes. This results from the ordered assembly of polar units giving rise to collective electrostatic effects. Interestingly, the latter have also been shown to impact the core level energies of the POMs [1]. Consequently, these effects, reflected as electrostatic shifts, can be conveniently monitored by X-ray photoelectron spectroscopy (XPS) [2-4]. For core-level excitations from atoms close to the substrate, the situation becomes more involved, as adsorption-induced charge rearrangements can also give rise to chemical shifts. In this contribution we present density functional theory (DFT) calculations for such cases. They allow a reliable interpretation of XPS data by addressing the interplay of chemical and electrostatic shifts. Our analysis highlights how the combination of DFT and XPS works as a powerful tool for the investigation of electronic and also structural properties of interfaces. [1] Taucher et al., *J. Phys. Chem. C*, 2016, 120, 3428. [2] Sauter et al., *J. Phys. Chem. C*, 2018, 122, 19514. [3] Hehn et al., *J. Phys. Chem. Lett.*, 2016, 7, 2994. [4] Cabarcos et al., *J. Phys. Chem. C*, 2017, 121, 15815.