

## O 54: Organic Molecules on Inorganic Substrates III: Magnetism, Doping and Interfaces

Time: Wednesday 10:30–13:00

Location: H24

O 54.1 Wed 10:30 H24

**Jahn-Teller Splitting in Single Adsorbed Molecules Revealed by Isospin-Flip Excitations** — ●M. BÖHME<sup>1</sup>, J. KÜGEL<sup>1</sup>, P.-J. HSU<sup>1</sup>, K. SCHNEIDER<sup>1</sup>, J. SENKPIEL<sup>1</sup>, D. SERRATE<sup>2</sup>, M. BODE<sup>1</sup>, and N. LORENTE<sup>3</sup> — <sup>1</sup>Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Germany — <sup>2</sup>Instituto de Nanociencia de Aragon & Departamento Física Materia Condensada, University of Zaragoza, Spain — <sup>3</sup>Centro de Física de Materiales & Donostia International Physics Center, San Sebastian, Spain

In the past decades, the spin Kondo effect was subject of numerous studies [1]. Its hallmark is a resonance at the Fermi level which emerges from the screening of a spin-degenerate localized orbital and splits in an external magnetic field and leads to inelastic spin-flip excitations. In this study, we report on the observation of an unusual spatial variation of the inelastic STS signal observed on single MnPc molecules adsorbed on ( $\sqrt{3} \times \sqrt{3}$ ) surface alloys of post-transition metals with noble metal fcc(111) surfaces. On these distorted molecules we measure tunneling spectra which are characterized by abrupt rises of the conductance at either positive or negative bias polarity depending on the tip position. The results are interpreted in terms of a Jahn-Teller effect which lifts the orbital degeneracy and leads to an isospin- or pseudospin-flip excitation, the inelastic analogue of an orbital Kondo resonance [2].

[1] M. Ternes *et al.*, *J. Phys. Condens. Matter* **21**, 053001 (2009).

[2] J. Kügel *et al.*, *Phys. Rev. Lett.* **21**, 226402 (2018).

O 54.2 Wed 10:45 H24

**Aromaticity of Contracted Porphyrins: Surface Reactivity of an Adsorbed Corrole** — ●JAN HERRITSCH<sup>1</sup>, JAN-NICLAS LUY<sup>1</sup>, MALTE ZUGERMEIER<sup>1</sup>, FALK NIEFIND<sup>1</sup>, BENEDIKT P. KLEIN<sup>1</sup>, MARTIN SCHMID<sup>1</sup>, PETER SCHWEYEN<sup>2</sup>, MARTIN BRÖRING<sup>2</sup>, RALF TONNER<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, TU Braunschweig, Germany

Corroles belong to the family of cyclic tetrapyrroles. As such, they are related to the well-studied porphyrins, from which they differ by one missing methine bridge and a direct pyrrole-pyrrole link. Thus, they can be described as contracted porphyrins. This small structural difference results in substantial changes, in particular of the delocalized  $\pi$ -electron system. Here, we present a study of the on-surface dehydrogenation reaction of corroles. We have investigated monolayers of an octaalkyl-substituted free-base corrole on Ag(111) and Cu(111) surfaces. The adsorbed molecule contains one labile pyrrolic N-H bond, which dissociates already below 230 K on Ag(111). The barrier of this dehydrogenation was estimated by DFT calculations and is consistent with our experimental results. The valence electronic structure was further characterized by UPS and compared to DFT calculations. The dehydrogenated species, although formally a radical, has almost no remaining spin density in the adsorbed state. By applying the fundamental concepts of aromaticity and electron delocalization, this finding can be explained by charge transfer from the surface to the molecule, so that the aromatic  $18\pi$  electron system is retained.

O 54.3 Wed 11:00 H24

**Study of 12-Metallacrowns-4 Complexes** — ●ROBERT RANECKI<sup>1</sup>, SWEN EHNERT<sup>1</sup>, BENEDIKT BAUMANN<sup>1</sup>, YAROSLAV PAVLYUKH<sup>1</sup>, GEORG LEFKIDIS<sup>1</sup>, WOLFGANG HUBNER<sup>1</sup>, ANGELIKI ATHANASOPOULOU<sup>2</sup>, EVA RENTSCHLER<sup>2</sup>, STEFAN LACH<sup>1</sup>, and CHRISTIANE ZIEGLER<sup>1</sup> — <sup>1</sup>Department of Physics, TU Kaiserslautern, Erwin-Schrodinger-Strasse 46, 67663 Kaiserslautern — <sup>2</sup>Institute of inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz

Organometallic multi spin centers and the orientation of the resulting molecular spin moment break new ground for future applications. In this context, the metallacrown complexes (MC) represent an exceptional class of coordination compounds. In most cases MCs decompose by thermal evaporation which is typically used for ultra-high vacuum preparation. Here, we present the preparation of the 12-MC-4 complex (HNEt<sub>3</sub>)<sub>2</sub>[CuCu<sub>4</sub>(shi)<sub>4</sub>] on different substrates by e-spray, avoiding a defragmentation of the molecules. Using state-of-the-art quantum-chemistry (beyond the Goodenough-Kanamori rules) enables us to identify the spin split d-states in situ prepared CuCu<sub>4</sub> MC and

the electronic molecular structure by photoelectron spectroscopy. For observing metal substrate induced collective spin phenomena we use the hybrid system CuCu<sub>4</sub>/Cu(100). STM/STS investigations show electronic properties and the adsorption orientation of the CuCu<sub>4</sub> molecules related to the lattice of Cu(100).

O 54.4 Wed 11:15 H24

**The Mixed Localization of Doping-Induced Charge Transfer at Semiconductor/Organic Interfaces: F4TCNQ on ZnO(10-10)** — ●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 types, usually depending on the nature of the substrate. On metals, where the adsorbate often hybridizes with the substrate, hybrid bands are formed. These leads to a uniform, fractional charging of the organic overlayer. 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 work, we use DFT to study the charge distribution in an F4TCNQ monolayer adsorbed on the mixed terminated ZnO surface. Interestingly, we find that both mechanisms appear simultaneously for this system. Upon adsorption, the cyano groups of the molecule bind covalently to surface Zn atoms. The involved molecular orbitals hybridize with the substrate, leading to a homogeneous fractional positive charging of the molecular layer. Introducing free charge carriers in the substrate (e.g. by doping) additionally results in charge transfer of integer electrons into the unhybridized LUMOs of individual molecules. The fraction of molecules with filled LUMOs thereby directly depends on the charge carrier concentration in the ZnO. We conclude that hybridization of the orbitals, and not the "metallicity" of the substrates, determines the charge transfer mechanism.

O 54.5 Wed 11:30 H24

**Optoelectronic Properties of Hybrid Systems of Silicon and the Organic Semiconductor Copper-Hexadecafluorophthalocyanine** — ●ANNA STADLBAUER, HANNAH SCHAMONI, and MARTIN STUTZMANN — Walter Schottky Institut, TUM, Garching, Germany

Hybrid systems of organic and inorganic semiconductors combine these two materials in order to benefit from their complementary material properties, e.g. for semiconducting devices like solar cells. Therefore, a detailed knowledge of the electronic properties of the interface between the organic and the inorganic semiconductor is necessary. The organic semiconductor chosen in this work, copper-hexadecafluorophthalocyanine (F<sub>16</sub>CuPc), is air-stable and exhibits n-type semiconducting behavior, and its structural and morphological properties have been investigated by many groups. Besides, several studies have investigated the interaction between metals or other organic semiconductors and F<sub>16</sub>CuPc. Here, thin films of F<sub>16</sub>CuPc are deposited on silicon substrates of different doping types and doping concentrations in an organic molecular beam setup. The resulting hybrid systems are characterized amongst others by current-voltage and Kelvin Probe Force Microscopy measurements. Based on these data, we show the influence of doping concentration and type of the Si substrate on the optoelectronic properties of the hybrid heterojunctions.

O 54.6 Wed 11:45 H24

**Influences of potassium-intercalation on molecular properties: DBP on Ag(111)** — ●FELIX OTTO<sup>1</sup>, TINO KIRCHHUEBEL<sup>1</sup>, ANU BABY<sup>2</sup>, BERND SCHROETER<sup>1</sup>, ROMAN FORKER<sup>1</sup>, GUIDO FRATESI<sup>3</sup>, and TORSTEN FRITZ<sup>1</sup> — <sup>1</sup>Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany — <sup>2</sup>Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi 55, 20125 Milano, Italy — <sup>3</sup>ETSF and Dipartimento di Fisica, Università degli Studi di Milano, Via Celoria, 16, 20133 Milano, Italy

The polycyclic aromatic hydrocarbon tetraphenyldibenzoperiflanthene (DBP, C<sub>64</sub>H<sub>36</sub>) has advantageous properties for applications in the field of organic electronics. These are a consequence of its chemical structure consisting of an aromatic backbone with four phenyl rings nearly perpendicular to the molecular plane. We are interested in the

effect of potassium intercalation on the structural, optical, and electronic properties of DBP adsorbed on Ag(111). Several structurally reordered stable bonding stages were obtained with K doping. LEED and STM measurements combined with differential reflectance spectroscopy (DRS) as well as XPS and UPS including photoelectron momentum maps (PMMs) were used to investigate the system and yield a variety of different information. These results can only be interpreted unambiguously with the help of DFT calculations. We find that the added K atoms adsorb below the molecule and thereby obstruct the bonding channels between DBP and Ag. A gradual occupation of the DBP LUMO is also observed due to charging by K atoms.

O 54.7 Wed 12:00 H24

**Determining Dispersion Relations of strong coupling Metal/Organic Hybrid Structures** — ●MAXIMILIAN RÖDEL<sup>1</sup>, THOMAS STARK<sup>2</sup>, JOCHEN MANARA<sup>2</sup>, and JENS PFLAUM<sup>1,2</sup> — <sup>1</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>2</sup>Bavarian Center for Applied Energy Research (ZAE Bayern), 97074 Würzburg

Light matter interaction has been in the focus of intense research in recent years because of its feasibility of tuning the optical properties of sub-wavelength devices and interfaces. In particular, combining nanostructured metallic surfaces with organic semiconducting layers, new coupling phenomena emerge. In this contribution, we investigate the dispersion relations of plexcitons, i.e. of strongly coupled surface plasmons at metallic interfaces and localized excitonic states within a molecular adsorbant layer. For this purpose F<sub>16</sub>ZnPc layers have been chosen due to their strong emission enhancement in close proximity to suited metal surfaces [1]. We demonstrated that the momentum dependent Eigenstates and related energies of the detected plexcitons provide detailed insights in the microscopic characteristics such as coupling strength of  $\approx 100$  meV or effective interface dielectrics. Furthermore, the role of morphology on the plexciton dispersion is examined by comparing polycrystalline and single crystalline organic layers allowing for an evaluation of their respective potential for innovative opto-electronic devices.

[1] V. Kolb, J. Pflaum, Opt. Express 25 (2017) 6678

O 54.8 Wed 12:15 H24

**Addressing the NTCDA/Ag(111) interface state in large unit cells within ab-initio calculations** — ●LUKAS ESCHMANN, PETER KRÜGER, and MICHAEL ROHLFING — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, 48149 Münster, Germany

Molecular adsorption causes interaction between the electronic structure of adsorbate and substrate. One particular case is the energy shift of the Shockley surface state on Ag(111) and other surfaces: upon adsorption of organic molecules the state turns into an interface state leading to a change in dispersion and a shift to higher energy by as much as  $\sim 0.5$  eV.

Here we address the interface state between the Ag(111) surface and adsorbed NTCDA within density-functional theory (DFT). To identify the dispersion of the interface state we have developed a projection technique which maps the states of the adsorbate system onto the original Shockley state. The projection also handles the loss of the surface periodicity due to the adsorbate, thus recovering the parabolic dispersion of the interface state in its original periodicity. We find that the energy shift of the Shockley state, as well as changes of its

effective mass, are proportional to the adsorption coverage. Using our technique we also see a strong anisotropy in the dispersion of the state.

O 54.9 Wed 12:30 H24

**Critical Interplay of Atomic and Electronic Structure of Strong Electron Acceptors on Semiconductor Surfaces** — ●HAIYUAN WANG<sup>1</sup>, THORSTEN SCHULTZ<sup>2</sup>, SERGEY LEVCHENKO<sup>1</sup>, NORBERT KOCH<sup>2</sup>, MATTHIAS SCHEFFLER<sup>1</sup>, and MARIANA ROSSI<sup>1</sup> — <sup>1</sup>Fritz Haber Institute, Berlin, Germany — <sup>2</sup>Humboldt University, Berlin, Germany

In organic-inorganic interfaces, it is necessary to understand how the atomic and electronic degrees of freedom cooperate or compete to yield the desired functional properties. Here, we address this issue first for strong electron acceptors (F4-TCNQ and F6-TCNNQ) adsorbed on H-Si(111). We perform systematic structure searches using density-functional theory with the HSE06 functional augmented by many-body van-der-Waals corrections. The results show that despite their similar composition, F4-TCNQ and F6-TCNNQ adsorb with significantly different geometries and show island formation propensities consistent with Volmer-Weber and Stranski-Krastanov growth modes, respectively. These densely-packed geometries induce a large interface-charge rearrangement, corresponding to a work-function (WF) increase of 1.11 eV for F4-TCNQ and 1.76 eV for F6-TCNNQ. Interestingly, vibrational fluctuations at room temperature produce a wide distribution of WF values, well modelled by a normal distribution with  $\sigma=0.17$  eV [1]. Afterwards, we compare these results to the behavior of F6-TCNNQ on MoS<sub>2</sub>, where the origin of temperature-dependences in the charge transfer is discussed. This work is supported by the SFB-951 project. [1] H. Wang, *et al.*, arXiv:1811.00037 (2018)

O 54.10 Wed 12:45 H24

**Level Alignment in Large-Scale Hybrid Organic-Inorganic Systems from Hybrid Density Functional Theory** — ●SVENJA M. JANKE<sup>1</sup>, MARIANA ROSSI<sup>2</sup>, SERGEY V. LEVCHENKO<sup>3,2</sup>, MATTHIAS SCHEFFLER<sup>2</sup>, MANOJ K. JANA<sup>1</sup>, CHI LIU<sup>1</sup>, DAVID B. MITZL<sup>1</sup>, and VOLKER BLUM<sup>1</sup> — <sup>1</sup>Duke University, Durham, USA — <sup>2</sup>Fritz Haber Institute of the Max Planck Society, Berlin, GER — <sup>3</sup>Skolkovo Institute of Science and Technology, Moscow, RU

Hybrid organic-inorganic systems allow to combine the properties of organic and inorganic substances at the nanoscale and hence open up a wide area for design of new materials with tunable properties. The positions of carrier levels and their alignment determine electronic properties of hybrid materials. A key challenge is that the systems in question tend to be large, due to alignment of components with inherently different lattice parameters or due to complex crystal structure packing. We here use hybrid density functional theory (FHI-aims all-electron code) for systems comprising over 1,000 atoms to reliably predict level alignments in two types of systems. For the paradigmatic interface system tetracene and pentacene at H/Si(111), we demonstrate the necessity of choosing large cells that reflect the coincidence pattern and find type II heterojunction behavior with potential separation of charge between organic and inorganic component. For a layered double perovskite we demonstrate how level alignment between organic and inorganic compound is affected when the metal ion is exchanged, and rationalize experimentally observed photoluminescence in these systems. Supported by DFG-projects SFB-951, JA 2843/1-1; NSF 1728921.