

## O 22: Organic-Inorganic Hybrid Systems and Organic Films III

Time: Monday 17:00–18:30

Location: WIL A317

O 22.1 Mon 17:00 WIL A317

**Focused Electron Beam Induced Processing on Surface-Anchored Metal-Organic Frameworks** — ●MARTIN DROST<sup>1</sup>, LUISA BERGER<sup>1</sup>, FAN TU<sup>1</sup>, CHRISTIAN PREISCHL<sup>1</sup>, HARTMUT GLIEMANN<sup>2</sup>, CHRISTOF WÖLL<sup>2</sup>, and HUBERTUS MARBACH<sup>1</sup> — <sup>1</sup>Physik. Chemie II, FAU Erlangen-Nürnberg, GER — <sup>2</sup>Institut f. funktionelle Grenzflächen, KIT, GER

We demonstrate the feasibility of Focused Electron Beam Induced Processing (FEBIP) techniques on Surface-Anchored Metal-Organic frameworks (SURMOFs)1 to lithographically fabricate nanostructures. These are: Electron Beam Induced Deposition (EBID)2, in which adsorbed precursor molecules are locally dissociated by the impact of the electron beam, leaving a deposit on the surface, and Electron Beam Induced Surface Activation (EBISA)3, where the substrate is locally activated by the e-beam in the absence of a precursor, such that a subsequently dosed precursor is catalytically decomposed at these sites and forms a deposit. Both approaches were conducted with Fe(CO)5 and Co(CO)3NO on HKUST-1 and a porphyrin-based SURMOF. We show that Fe(CO)5 is suitable for EBID and EBISA on both SURMOFs, whereas Co(CO)3NO works solely for EBID but is not susceptible to EBISA. We also demonstrate the possibility to fabricate nanostructures with linewidths <10 nm. All deposits were characterized with Scanning Electron Microscopy (SEM) and local Auger Electron Spectroscopy (AES). Supported by the DFG through grant MA 4246/1-2, research unit FOR 1878/funCOS; COST Action CM1301; Excellence Cluster EAM of the FAU Erlangen-Nürnberg.

O 22.2 Mon 17:15 WIL A317

**Electronic structure of magnesiumtetraphenylporphyrin on MgO** — ●REBECCA PÖSCHEL, GIANLUCA DI FILIPPO, and THOMAS FAUSTER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7, 91058 Erlangen

Ultrathin films of magnesium oxide (MgO) covered with magnesium tetraphenylporphyrin (MgTPP) were grown in-situ on a Ag(100) single crystal. The layer thickness of MgTPP was varied as well as the layer thickness of MgO underneath. The influence of the substrate and of the MgTPP layer thickness on the occupied and unoccupied molecular orbitals were investigated using photoelectron spectroscopy. With vacuum ultra-violet photoelectron spectroscopy (photon energy 21.2 eV) the occupied orbitals were studied and for the unoccupied orbitals two-photon photoelectron spectroscopy was used (photon energies of 3.06 eV - 3.16 eV and 4.59 eV - 4.76 eV). We found a HOMO-LUMO gap of around 4 eV similar to previous measurements on Ag(100).

O 22.3 Mon 17:30 WIL A317

**Optimization and experimental investigation of hybrid organic-inorganic (plasmon-) nanolaser designs** — ●MARTIN ROTHE, GÜNTER KEWES, and OLIVER BENSON — Humboldt-Universität zu Berlin, Department of Physics, Nanooptics Group, Newtonstraße 15, 12489 Berlin, Germany

The understanding of coherent scattering, amplification and lasing in nanoscopic structures is essential for future optical and optoelectronic devices. Due to their nonlinear threshold behaviour, lasing systems could be used as active building blocks or fast modulators in such devices. However this requires a deeper understanding of the interplay between gain medium and resonators. We focus on hybrid nanolaser designs consisting of inorganic resonators and organic gain medium.

In order to optimize those structures we study various nanoresonator geometries and materials. Therefore we investigate both, plasmonic nanowires (to build a spaser) and dielectric resonators (to build a nanolaser). The nanostructures are analyzed in our optical setup, allowing for spatial, spectral and temporal analysis of single systems as well as ensembles, various illumination/excitation geometries, including dark field imaging as well as confocal scanning. In parallel we use numerical simulations to validate our experimental findings and to optimize the designs.

O 22.4 Mon 17:45 WIL A317

**Molecular Topology and Surface Chemical Bond: Alternant vs. Non-Alternant Aromatic Molecules** — ●BENEDIKT P. KLEIN<sup>1</sup>, NADINE VAN DER HEIJDEN<sup>2</sup>, CLAUDIO K. KRUG<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

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The interaction of conjugated organic molecules, in particular aromatic species, with metal surfaces has been a major topic in surface science. So far, the focus has almost exclusively been on molecules with alternating topologies such as pentacene. These molecules have a uniform charge distribution and highly delocalized frontier orbitals. In contrast, non-alternant topologies cause non-uniform charge distributions, and more localized frontier orbitals. We present the first systematic studies of naphthalene and its non-alternant counterpart azulene on the (111) surfaces of Cu and Ag. On the basis of extensive PES, NEXAFS, TPD, nc-AFM and STM studies, we show that the non-alternant topology results in much stronger interaction with metal surfaces, especially in the case of Cu(111), and that the interaction is more localized. Periodic DFT calculations provide insight into the surface chemical bond and charge redistribution between surface and molecule. A major part of the localized interaction is the donation of electron density in the molecular LUMO. This leads to a considerable in-plane and out-of-plane deformation of the adsorbed non-alternant species.

O 22.5 Mon 18:00 WIL A317

**Global Structure Search for Organic/Inorganic Interfaces: TCNE on Au(111)** — ●VERONIKA OBERSTEINER, MICHAEL SCHERBELA, LUKAS HÖRMANN, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

Structure determination at organic/inorganic interfaces is highly challenging. As individual experiments often convey partial or ambiguous information, computational simulations become increasingly important to aid the interpretation. Here, we demonstrate the power of theoretical polymorph prediction on the example of TCNE (tetracyanoethene) on Au(111).

Predicting polymorphs from first principles is far from trivial. The main challenge is the vast configurational space, i.e. the number of different polymorphs raising exponentially with the number of molecules in the unit cell. Here, we present an approach based on a discretization of the potential energy surface (PES), where we first determine the local adsorption geometries and afterwards span the PES as combinations of these. Dispersion corrected density functional theory is then applied for optimization and to obtain their relative energies.

Applying this approach to TCNE/Au(111), we predict the global minimum to be an ordered triangular structure of slightly tilted upright standing molecules with a substrate adatom in the center. The existence of the adatom cannot be inferred from experimental STM alone [1], but we find it crucial to be able to reproduce the experiment. [1] D. Wegner et al. Nano Letters, 8, 131-135, 2008.

O 22.6 Mon 18:15 WIL A317

**How a functionalization with cyano groups modifies the adsorption behavior and reactivity of 2H-tetraphenylporphyrin on Cu(111)** — MICHAEL LEPPER<sup>1</sup>, MANUEL MEUSEL<sup>1</sup>, JULIA KÖBL<sup>1</sup>, LIANG ZHANG<sup>1</sup>, MICHAEL STARK<sup>1</sup>, ABNER DE SIERVO<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and ●HUBERTUS MARBACH<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 — <sup>2</sup>Institute of Physics, Gleb Wataghin, University of Campinas (UNICAMP), Campinas, SP, Brazil

We studied the adsorption behavior of 2H-tetraphenylporphyrin (2HTPP) with 1, 2 and 4 cyano-functionalized phenyl groups on Cu(111) by means of room temperature scanning tunneling microscopy (STM) in ultra-high vacuum. While 2HTPP adsorbs as individual isolated molecule [1], the cyano-functionalized porphyrins form dimers or 1-D molecular chains after mild annealing, depending on the number and geometry of the attached cyano groups. Thereby, the main binding motives are Cu adatoms, which appear to act as linkers between cyano groups of neighboring molecules. In addition, we observe self-metalation [2,3], that is, the metalation of the porphyrin macrocycle with Cu atoms from the substrate. Interestingly, the yield of this reaction is strongly affected by the actual cyano-functionalization, which goes along with the differences in the adsorption behavior of the porphyrin derivatives.

[1] F. Buchner et al., J. Phys. Chem. C, 115 (2011) 24172 [2] K. Diller et al., J. Chem. Phys., 136 (2012) 014705 [3] H. Marbach, Acc. Chem. Res., 48 (2015) 2649