

O 58: Organic-Inorganic Systems III: Metal-Organics

Time: Wednesday 15:00–18:00

Location: S054

O 58.1 Wed 15:00 S054

Oxidation State Tuning in Ligand-Metal Surface Reaction: Formation of M(III)-Corroles on Ag(111) — ●MALTE ZUGERMEIER¹, NICOLAS BOCK¹, MIN CHEN¹, FALK NIEFIND¹, JAN HERRITSCH¹, LUKAS RUPPENTHAL¹, MARTIN SCHMID¹, PETER SCHWEYEN², MARTIN BRÖRING², and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Germany

Surface-supported planar metal complexes are of high technical interest for catalytic applications combining the advantages of heterogeneous and homogeneous catalysis. However, a high degree of control over the chemical and electronic properties of the metal centers is required. While this control can be achieved by the attachment of axial ligands, these ligands compete with the reactants for the axial coordination site. Therefore, a more suitable solution is achieved by modification of the planar ligand. We demonstrate that adsorbed corroles on Ag(111) oxidize metal atoms to their +III state and form the corresponding metal complexes. In contrast, adsorbed porphyrins and phthalocyanines can oxidize co-adsorbed metal atoms only to +II ions. Corroles differ from the closely related porphyrins by the absence of a single carbon atom in the macrocycle. The resulting size-reduced ring provides a tighter coordination environment and stabilizes higher oxidation states. Specifically, we studied monolayers and multilayers of an octa-alkyl corrole and their reaction with Ni and Co atoms on a Ag(111) surface by XPS, UPS and STM.

O 58.2 Wed 15:15 S054

Molecular adsorption and self-assembled structures of tetra(cyanophenyl)porphyrin on Cu(111) and ultrathin CoO as substrate — ●TOBIAS SCHMITT, MARCO RASCHMANN, LUTZ HAMMER, and M. ALEXANDER SCHNEIDER — Solid State Physics, University Erlangen-Nürnberg, 91058 Erlangen, Germany

Molecular self-assembly on surfaces is controlled by a complex balance between molecule-substrate and intermolecular interactions. We report on the adsorption geometry of single molecules and ordered phases of free-base meso-tetra(m-cyanophenyl)porphyrin (TCNPP) on Cu(111) and on CoO(111)/Ir(100) thin films using low-temperature scanning tunneling microscopy in ultrahigh vacuum. The molecules were deposited at different substrate temperatures to activate diffusion and potential self-assembly processes. When depositing TCNPP onto the Cu(111) surface at T=293K intermolecular H-bonding and dipolar coupling are found to be the dominating inter-molecular interactions but extended ordered structures are not formed. Already at slightly higher temperatures 2-fold metal-ligand coordination comes into play and starts dominating the assembly of linear structures on Cu(111). The molecules themselves remain unmetalated. Also on thin CoO(111) films TCNPP molecules cluster into islands with little tendency to form ordered structures when adsorbed at T=293K. When heated to T=420K the TCNPPs surprisingly show a different internal structure in STM images akin to metalated molecules. At this temperature also networks are observed that show a 3- or 4-fold coordination which we interpret as a sign of metal coordination at the CoO surface.

O 58.3 Wed 15:30 S054

Intermolecular interactions among TiOPc molecules on Ag(111) — ●LAURA FERNÁNDEZ¹, SEBASTIAN THUSSING¹, ANTON BRIÓN-RÍOS², PEPA CABRERA-SAN FELIX², DANIEL SÁNCHEZ-PORTAL³, and PETER JAKOB¹ — ¹Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany — ²DIPC, Paseo Manuel Lardizábal 4, 20018 San Sebastián, Spain — ³Centro de Física de Materiales CSIC-UPV/EHU, Paseo Manuel Lardizábal 5, 20018 San Sebastian, Spain

The structure and intermolecular interactions of TiOPc deposited on Ag(111) has been investigated by IR spectroscopy and SPA-LEED. Additionally, the structure and bonding strength of the TiOPc/Ag(111) system has been explored by DFT. According to IR data, deposition of TiOPc (sub)monolayers leads to a “TiO-up” adsorption geometry of the molecules on Ag(111). Moreover, we find unambiguous evidence for an attractive interaction between neighboring TiOPc molecules, which leads to the formation of 2D islands with well-defined long range order (c-phase) upon cooling (sub)monolayer films to temperatures below

70K. This behavior is ascribed to the dominance of van der Waals interactions between adsorbed TiOPc molecules, and it is in contrast to the intermolecular repulsion observed for the CuPc/Ag(111) system. Repulsive intermolecular interactions induced by the parallel oriented dipoles of the TiO groups are negligible presumably due to the large lateral molecular dimensions. According to DFT calculations, the molecule-metal interaction of TiOPc on Ag(111) is notably weaker than in the case of CuPc, and it is lacking any net charge transfer.

O 58.4 Wed 15:45 S054

A new perspective on the adsorption behavior of nonplanar phthalocyanines on Cu(111) — ●ELISABETH WRUSS¹, SHASHANK S. HARIVYASI¹, DAVID A. EGGER², OLIVER T. HOFMANN¹, ELISABETH VERWUESTER¹, ALEXANDER GERLACH³, NAHID ILYAS⁴, FRANK SCHREIBER³, OLIVER L. A. MONTI⁴, and EGBERT ZOJER¹ — ¹Graz University of Technology, Graz, Austria. — ²Weizmann Institute of Science, Rehovoth, Israel. — ³Universität Tübingen, Tübingen, Germany — ⁴University of Arizona, Tucson, USA

The geometric and electronic properties of nonplanar, chlorinated members of the phthalocyanine family, namely chlorogallium phthalocyanine and chloroboron subphthalocyanine upon adsorption on Cu(111) are investigated, using DFT simulations including the vdW-surf correction. The comparison with experimental results including x-ray standing wave, ultraviolet photoelectron spectroscopy and scanning tunneling microscopy yields strong indications of a dissociation of the molecules upon adsorption associated with a loss of the Cl atom as one possible scenario. For the chlorogallium phthalocyanine system, the experimental and calculated adsorption heights and adsorption-induced work-function shifts yield good quantitative agreement. Surprisingly, the same work-function change is also found for the adsorption of intact “Cl-down” molecules, despite hugely different geometries and molecular dipoles. This seeming contradiction can be explained as a consequence of Fermi-level pinning. Our findings show that the adsorption process of chlorinated phthalocyanines and related molecules is considerably more complex than previously assumed.

Invited Talk

O 58.5 Wed 16:00 S054

Thin Films of Metal-Organic Frameworks: Functional, photoswitchable coatings and unique model systems — ●LARS HEINKE — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Deutschland

Metal-organic frameworks (MOFs) are nanoporous, crystalline materials, assembled from metal nodes and organic linker molecules. In addition to many potential applications of the (conventional) powder MOF material, well-defined thin films seem perfectly suited for challenging uses and as unique model systems, where certain molecular and MOF properties can be precisely measured by applying surface sensitive techniques. These thin films are prepared in a layer-by-layer fashion on a solid substrate by using liquid-phase epitaxy, referred to as the SURMOF-approach.

Incorporating photochromic molecules like azobenzene in the crystalline structure enables the switching of physical and chemical MOF properties by light. This can be used for various uses, such as realizing the remote-controlled release of guest molecules from a nanoporous container.

These thin films also enable detailed investigations of the molecules which are incorporated in the crystalline structure, unlike investigating these molecules in solution. In this way, the isomerization of isolated azobenzene moieties could be investigated.

Recently, the electronic structure and electrical properties of MOFs have become a research focus. SURMOFs have been used to investigate the direction-dependent conductivity in anisotropic MOF structures.

O 58.6 Wed 16:30 S054

Tetrapyrrole metalation with rare earths — ●KATHARINA DILLER¹, APARAJITA SINGHA¹, CHRISTIAN WÄCKERLIN¹, JAN DREISER², ALBERTO VERDINI³, ALBANO COSSARO³, LUCA FLOREANO³, and HARALD BRUNE¹ — ¹École Polytechnique Fédérale de Lausanne, Switzerland — ²Paul Scherrer Institute, Switzerland — ³CNR-IOM, Laboratorio Nazionale TASC, I-34149 Trieste, Italy

The *in vacuo* metalation of tetrapyrrole molecules is a convenient way to build tetrapyrrole-based metal-organic structures on metal surfaces.

A commonly employed route is the deposition of molecules by organic molecular beam epitaxy, which subsequently are exposed to a beam of metal atoms. Given the importance of terbium phthalocyanine double decker compounds as single molecule magnets, it is surprising that so far on-surface metalation predominantly focused on the creation of transition metal complexes, with only few scanning tunneling microscopy (STM) studies dedicated to the rare earth Ce [1, 2]. Here, we follow the metalation of free-base tetraphenylporphyrin and free-base phthalocyanine molecules on Ag(111) with different rare earth metals using a combination of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy. We show that metalation can be readily achieved at room temperature, and discuss the effects of an excess of metal atoms on the spectroscopic signatures.

[1] D. Ćcija *et al.*, *Angew. Chem. Int. Ed.*, 2011, 50, 3872, [2] A. Weber-Bargioni *et al.*, *J. Phys. Chem. C*, 2008, 112, 3453.

O 58.7 Wed 16:45 S054

Electric transport properties of pristine and loaded surface-anchored metal-organic frameworks — JIANXI LIU¹, TOBIAS WÄCHTER², ANDREAS IRMLER³, PETER G. WEIDLER¹, HARTMUT GLIEMANN¹, FABIAN PAULY³, VERONICA MUGNAINI¹, MICHAEL ZHARNIKOV², and CHRISTOF WÖLL¹ — ¹Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany — ²Applied Physical Chemistry, University of Heidelberg, 69120 Heidelberg, Germany — ³Department of Physics, University of Konstanz, 78457 Konstanz, Germany

Understanding of the electric transport through surface-anchored metal-organic frameworks (SURMOFs) is important both from a fundamental perspective as well as with regards to possible future applications in electronic devices. To address this mostly unexplored subject, we integrated a series of representative SURMOF thin films, formed by copper nodes and trimesic acid and known as HKUST-1, in a mercury-drop based tunneling junction. Although the transport properties of these SURMOFs are analogous to those of hybrid metal-organic molecular wires, manifested by a very low value of the tunneling decay constant ($\beta = 0.006$ 1/Å), they are at the same time found to be consistent with a linear increase of resistance with film thickness. Upon loading of SURMOF pores with ferrocene or tetracyanoquinodimethane (TCNQ), a noticeable increase in transport current was observed, being especially dramatic (6 orders of the magnitude) in the case of TCNQ. Relevant structural and transport models are discussed.

O 58.8 Wed 17:00 S054

Synthesis of Organometallic Sandwich Complexes and Nanowires on Graphene — FELIX HUTTMANN, NICOLAS SCHLEHECK, MERVE SEÇKIN, and THOMAS MICHELY — II. Physikalisches Institut, Universität zu Köln, Zùlpicher Straße 77, 50937 Köln, Germany

Organometallic sandwich-molecular nanowires of europium-cyclooctatetraene (EuCot) and vanadium-benzene (VBz) have been theoretically predicted to have interesting electronic structures: Semiconducting and ferromagnetic (EuCot) [1] or half-metallic and ferromagnetic with full spin polarization of the conduction band (VBz) [2]. They thus have potential for efficient spin filters. Here, we have pursued their growth from the constituent vapors on an inert graphene surface, and investigated the samples *in situ* using scanning tunneling microscopy. EuCot nanowires form readily, and by varying the growth conditions, we find a rich spectrum of morphologies, from a disordered, spaghetti-like growth to highly ordered, anisotropically shaped, two-dimensional crystallites made of wire bundles. In these bundles, the wires are offset against their nearest neighbors to allow the wires to hook into each other, and where wire bundles bend, a characteristic bending angle is often observed to accommodate this. In contrast, for VBz only sandwich molecules of composition VBz₂ could be produced, but no wires. VBz₂ molecules form overlayers and desorb at around room temperature.

[1] Ke Xu *et al.*, *J. Chem. Phys.* 131, 104704 (2009)

[2] V. V. Maslyuk *et al.*, *Phys. Rev. Lett.* 97, 097201 (2006)

O 58.9 Wed 17:15 S054

Metalation of porphyrin with Mg on Ag(100) — GIANLUCA DI FILIPPO, ANDREJ CLASSEN, REBECCA PÖSCHEL, and THOMAS FAUSTER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7, 91058, Erlangen, Germany

Porphyrins are a class of π -conjugated organic molecules of high technological interest. Their optical, electronic and chemical properties make them very suitable for energy production in solar cells, phototherapy, and catalysis [1]. Porphyrins are composed of a macrocycle of four pyrrole rings (C₄H₄N-) connected by methine units (=CH-). The nitrogen atoms at the interior form a central pocket ideal to incorporate metal atoms and to obtain metal-porphyrins by direct metalation of molecules adsorbed on inert metal surfaces [2].

Using X-Ray photoelectron spectroscopy (XPS) we investigated the *in situ* metalation of one monolayer tetraphenylporphyrin (2HTPP) on Ag(100) with Mg atoms. This reaction results in the formation of adsorbed magnesium(II)-tetraphenylporphyrin (MgTPP). The metalation is observed to take place either by evaporating Mg atoms on top of the 2HTPP monolayer or by depositing 2HTPP on top of the Ag surface with adsorbed Mg atoms. In the second case, the presence of oxygen contamination and consequent MgO formation reduces the efficiency at which Mg atoms are embedded in the molecule macrocycle.

[1] W. Auwärter *et al.*, *Nature Chemistry*, 7, 105 (2015)

[2] J.M. Gottfried *et al.*, *J. Am. Chem. Soc.*, 128, 5644 (2006) - F. Buchner *et al.*, *J. Phys. Chem. C*, 112, 15458 (2008)

O 58.10 Wed 17:30 S054

Metalation of porphyrins on metal and oxide surfaces — OLE LYTKEN, MICHAEL RÖCKERT, MATTHIAS FRANKE, DANIEL WECHSLER, QURATULAIN TARIQ, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg

Porphyrins are large conjugated organic molecules with four pyrrole units capable of coordinating either two protons or a metal ion in the center of the molecule. Both metalated and unmetalated molecules can be deposited on surfaces under ultrahigh vacuum using physical vapor deposition. However, once deposited the unmetalated molecules might react with the substrate they have been deposited on and metalate. We have studied this self-metalation reaction of 5,10,15,20-tetraphenylporphyrin (2HTPP) on Cu(111), a metal surface, and MgO(100), an oxide surface. On both surfaces the reaction with the substrate occurs at, or slightly above, room temperature, forming CuTPP and MgTPP, respectively. The project is supported by the DFG through FOR 1878 (funCOS).

O 58.11 Wed 17:45 S054

Surface-assisted reactions of porphyrins investigated by nc-AFM — JACOB DUCKE, YUANQIN HE, FELIX BISCHOFF, MANUELA GARNICA, and WILLI AU — TU München, Germany

Surface-assisted covalent linking of precursor molecules enables the fabrication of low-dimensional nanostructures. Here, we present a temperature-induced covalent dehydrogenative coupling mechanism of free-base porphine (2H-P) units. The oligomers resulting from a homocoupling reaction have been characterized by a multitechnique approach and theoretical modelling, however an atomically resolved study of the resulting nanostructures was lacking [1]. With nc-AFM we are able to identify the resulting bonding motifs and can confirm the proposed structural models. Furthermore, we used a similar coupling mechanism to functionalize the edges of epitaxially grown graphene on Ag(111) with 2H-P [2]. Distinct configurations are identified and resolved at the graphene edges with submolecular precision. Functionalization reactions like metallation of the 2H-P and subsequent axial ligation of adducts are conserved for porphines coupled to graphene. Thus, our findings bear promise for functionalized graphene nanostructures and for the formation of tailored oligomers on surfaces.

[1] Wiengarten, A., *et al.* "Surface-assisted dehydrogenative homocoupling of porphine molecules." *J. Amer. Chem. Soc.* 136 (2014): 9346-9354.

[2] He, Y., *et al.* "Fusing tetrapyrroles to graphene edges by surface-assisted covalent coupling." submitted