

O 12: Inorganic/Organic Interfaces: Growth II

Time: Monday 15:00–18:15

Location: MA 005

O 12.1 Mon 15:00 MA 005

Many-Body Dispersion Effects in the Adsorption of Atoms and Molecules at Metal Surfaces — ●VICTOR RUIZ and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der MPG, Theory Department, Berlin, Germany

Van der Waals (vdW) interactions play an essential role in the structure and stability of atoms and molecules adsorbed at inorganic surfaces. Several promising methods have been developed in recent years for an efficient modeling of these ubiquitous interactions in molecules and solids. However, most of these methods are still based on an effective pairwise treatment of vdW interactions, ignoring the often important many-body contributions to the vdW energy. Here we show that the inclusion of many-body effects in vdW interactions enables us to achieve quantitative predictions in the adsorption energies of atoms and molecules on metal substrates. For this, we employ the recently developed many-body dispersion method coupled with density-functional theory (DFT+MBD) [1,2], which includes many-body effects in the long-range correlation energy to all orders in the dipole approximation. We study the influence of MBD effects on the adsorption structures, energies, and perpendicular vibrational frequencies of a Xe monolayer on transition metal surfaces. We further study the adsorption of PTCDA ($C_{24}H_8O_6$) on Au(111), and compare to recent measurements of the adsorption energy and vertical adsorption height. [1] Phys. Rev. Lett. 108, 236402 (2012); [2] J. Chem. Phys. 140, 18A508 (2014).

O 12.2 Mon 15:15 MA 005

LEEM investigation of the initial growth of heteromolecular layers — ●CAROLINE HENNEKE¹, DANIEL SCHWARZ^{1,2}, and CHRISTIAN KUMPF¹ — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany, and Jülich Aachen Research Alliance (JARA)-Fundamentals of Future Information Technology — ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA

One crucial issue for the performance of organic materials in electronic devices is the ability to specifically design the interfaces between different active layers according to their functional purpose. Heteromolecular films are of highest interest in this context, in particular their initial growth and the structure formation of the first molecular layer since this layer acts as a template for further growth.

The molecules Copper-II-phthalocyanine (CuPc) and 3,4,9,10-perylene-tetra-carboxylic-acid dianhydride (PTCDA) form well-ordered molecular monolayer structures when deposited on Cu(001). We present details of the growth kinetics of the molecular films and their dependence on the temperature and molecular concentrations on the surface during the deposition process. The growth was investigated in situ with LEEM and the geometric structure with LEED.

O 12.3 Mon 15:30 MA 005

Structural and optical investigation of weakly interacting commensurate organic-organic interfaces in SnPc/PTCDA heterolayers on Ag(111) — ●MARCO GRUENEWALD, JULIA PEUKER, MATTHIAS MEISSNER, FALKO SOJKA, ROMAN FORKER, and TORSTEN FRITZ — Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, Jena 07743, Germany

We report on structural and electronic properties of highly-ordered ultrathin layers of the dye molecules 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and tin(II)-phthalocyanine (SnPc) stacked on Ag(111). The thin films have been structurally characterized by low energy electron diffraction (LEED) and low temperature scanning tunneling microscopy (LT-STM) as well as optically by in situ differential reflectance spectroscopy (DRS) [Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. 108, 34-68 (2012)]. Depending on the coverage and on the substrate temperature the SnPc adlayers on top of 1 ML PTCDA/Ag(111) form either three different commensurate registries (with each unit cell different in size and number of molecules) or show a 2D-gas-like behavior. By means of DRS we found that the molecules in all phases show monomer behavior pointing to a rather weak electronic interaction at the organic-organic interface in contrast to conclusions recently drawn for a similar commensurate heterointerface with CuPc instead of SnPc [PRL 108, 106103 (2012)]. Thus, commensurism at organic-organic interfaces cannot necessarily be linked to strong electronic interaction. Additionally, for SnPc films with thick-

nesses beyond 1 ML we found intermediate phases prior the formation of a SnPc bulk structure.

O 12.4 Mon 15:45 MA 005

Vibrational properties of stacked and intermixed (CuPc + PTCDA) layers on Ag(111) — ●SEBASTIAN THUSSING and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

The vibrational properties and thermal evolution of stacked and intermixed CuPc and PTCDA layers deposited on Ag(111) have been investigated using IR absorption spectroscopy, SPA-LEED, and TDS. For the mixed layers four different monolayer phases have been found depending on the CuPc:PTCDA ratio. Ordering of cold deposited layers sets in after annealing to 250 K and prevails up to 500 K. All mixed phases display characteristic spectroscopic signatures in vibrational spectra. The monolayer phases of CuPc and PTCDA show pronounced interfacial dynamical charge transfer (IDCT). Interestingly, IDCT is attenuated for mixed layers, especially for the respective minority species. This is attributed to energetic shifts of the partially filled 'former LUMO' as a result of intermolecular coupling (through metal charge transfer). For stacked (bi)layers thermal annealing leads to interlayer exchange for CuPc on PTCDA as well as for PTCDA on CuPc which we attribute to the extra energy gain provided by intermixing and charge transfer between the constituents within the monolayer. For PTCDA on CuPc intermixing is found already for $T > 200K$, while the reverse stacking is stable up to 450K.

O 12.5 Mon 16:00 MA 005

Heteroorganic layers of CuPc and PTCDA on the Ag(110) surface — ●KATHRIN SCHÖNAUER^{1,2}, SERGUEI SOUBATCH^{1,2}, and FRANK STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²JARA - Fundamentals of Future Information Technology, Germany

The application potential of organic semiconductors for molecular electronics makes them interesting for fundamental research. Layers consisting only of one type of molecules have been investigated extensively over the last decades. Layers consisting of two different types of organic molecules, e.g. CuPc and PTCDA on the Ag(111) surface [1], are now subject of experiments. In this case, not only the interaction between the metal and the organic substance but also the molecule-molecule interaction is in the focus of research. We present investigations on mixed layers of CuPc and PTCDA on the Ag(110) surface, which is meant to be more reactive than the Ag(111) surface. The lateral arrangement is studied by low temperature scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The analysis of local electronic properties was done using scanning tunneling spectroscopy (STS).

[1] Stadtmüller et al., PRL 108, (106103) 2012

O 12.6 Mon 16:15 MA 005

Single Iron-Phthalocyanine molecules on Fe/W(001): A non-contact atomic force microscopy study at low temperature in UHV — ●JOSEF GRENZ, ALEXANDER SCHWARZ, and ROLAND WIESENDANGER — Institute of Applied Physics, University of Hamburg, Jungiusstrasse 11, 20355 Hamburg, Germany

While magnetic exchange force microscopy (MExFM) has been achieved on various substrates [1,2], the detection of a magnetic signal stemming from a single molecule employing atomic force microscopy (AFM) has not been observed so far. Recent work on Cobalt-Phthalocyanine (CoPC) on Fe/W(110) utilizing spin-polarized scanning tunneling microscopy revealed a strong hybridization of the molecular orbitals and substrate 3d states depending on the molecular adsorption, which affects the magnetic properties of the molecule [3]. In this study we deposit single in the gas phase paramagnetic Iron-Phthalocyanine (FePC) molecules on Fe/W(001) and find 7 different adsorption geometries using non-contact atomic force microscopy (nc-AFM). Particularly, we were able to identify the adsorption sites of the central Fe ion for the different geometries on the antiferromagnetic Fe monolayer on W(001), which will influence the magnetic properties of the molecule in its adsorbed state.

[1] U. Kaiser *et al.*, Nature **446**, 522 (2008).[2] R. Schmidt *et al.*, Nano Lett. **9**, 200 (2009).[3] J. Brede *et al.*, Phys. Rev. Lett. **105**, 047204 (2010).

O 12.7 Mon 16:30 MA 005

Quantitative test of the “surface trans-effect” in an adsorbed metal-organic complex — ●PETER S. DEIMEL¹, DAVID A. DUNCAN¹, TIEN-LIN LEE², LUKE A. ROCHFORD³, PARDEEP K. THAKUR², D. PHIL WOODRUFF³, FRANCESCO ALLEGRETTI¹, and JOHANNES V. BARTH¹ — ¹Physics Department E20, TU München, Germany — ²Diamond Light Source, Didcot, UK — ³University of Warwick, Coventry, UK

On-surface coordination chemistry is an emerging field, which holds promise for nanotechnology, molecular spintronics and catalysis [1]. Previous work provided evidence for a “surface trans-effect” where the interaction [2] and even the magnetic coupling [3] between the metal ion of adsorbed metal-organic species and the underlying substrate can be affected by ligation in *trans* position. Corresponding marked changes in height of the metal center with respect to the substrate were theoretically predicted [2].

We present the first quantitative analysis of this effect using normal incidence X-ray standing waves. For iron phthalocyanine on Ag(111) we observe a distinct increase in height of the Fe ion upon *NH*₃ ligation, whereas the tetrapyrrole macrocycle is effectively unperturbed. Our results provide a test-bed for modeling schemes and structure-functionality correlations relevant for technological applications.

- [1] J. V. Barth, *Surface Science* **603** (2009), 1533;
- J. M. Gottfried and H. Marbach, *Z. Phys. Chem.* **223** (2009), 53.
- [2] W. Hieringer et al., *J. Am. Chem. Soc.* **133** (2011), 6206.
- [3] Ch. Wäckerlin et al., *Nat. Commun.* **1** (2010), 61.

O 12.8 Mon 16:45 MA 005

Adsorption of MoMo-Methyl on Cu(111) — ●JOBYNSON KOLLAMANA¹, BENJAMIN STADTMÜLLER¹, JOHANNES STÖCKL¹, ANNEKEN GRÜN², MANUEL ZIMMER², MARKUS GERHARDS², MIRKO CINCHETTI¹, and MARTIN AESCHLIMANN¹ — ¹Department of Physics and Research Center Optimas — ²Department of Chemistry, University of Kaiserslautern

Metal-organic compounds are promising materials for new types of spintronic devices. While the magnetic and electronic properties of organic molecules in the gas phase are well understood, their behavior on metallic surfaces strongly depends on the interaction in these systems. Therefore, we studied the geometric and electronic properties of (sub)monolayer films of Molybdenum(II) acetate dimer (MoMo-Methyl) adsorbed on Cu(111) by scanning tunneling microscopy and complementary techniques.

For coverages below 1.0ML, the MoMo-Methyl molecules arrange in chains, oriented along high symmetry directions of the Cu(111) surface. Increasing the coverage to one monolayer results in the formation of long range ordered structures with domain sizes of several micrometers.

In addition, the electronic properties of these films were studied by scanning tunneling spectroscopy and photoelectron spectroscopy. Comparing these results to predictions for free MoMo-Methyl molecules allow to reveal the influence of the molecule-substrate interaction on the molecular properties.

O 12.9 Mon 17:00 MA 005

Temperature-driven demixing of a two-dimensional metal-organic network — ●RICO GUTZLER¹, SÖREN KROTZKY¹, CLAUDIUS MORCHUTT^{1,2}, VIJAY VYAS¹, BETTINA V. LOTSCH^{1,3}, and KLAUS KERN^{1,2} — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Switzerland — ³Ludwig Maximilians University and Center for Nanoscience, Munich, Germany

The great majority of reported surface-confined self-assembled molecular networks exhibit a crystalline structure. Under certain conditions, however, do non-crystalline networks form without long-range order, resembling two-dimensional glasses. Here we report a two-component metal-organic network that self-assembles at room temperature into such a glassy state on a crystalline surface. Scanning tunnelling microscopy reveals how an organic semiconducting molecule functionalized with two nitrile groups coordinates coadsorbed iron atoms to create a disordered porous layer. This binary mixture is then exposed to an annealing step, which upon cooling leads to the separation of the two components into spatially separate homogeneous and crystalline domains of either molecules or metal atoms. The first glassy state is thermodynamically not as stable as the second demixed state, although the demixing is accompanied by an entropy penalty equal to the entropy of mixing. The thermodynamic implications of this obser-

vation are discussed.

O 12.10 Mon 17:15 MA 005

Spectroscopic investigation of free base and Manganese 5,10,15-tris(pentafluorophenyl)corrole on Ag(111) — MA TEUSZ PASZKIEWICZ¹, ●STEFAN MÜLLEGER², UWE GERSTMANN⁴, HAZEM ALDAHAK⁴, EVA RAULS⁴, STEFANO TEBI², WOLFGANG SCHÖFBERGER³, WOLF GERO SCHMIDT⁴, REINHOLD KOCH², JOHANNES BARTH¹, and FLORIAN KLAPPENBERGER¹ — ¹TUM, Physik department E20, Garching, Germany — ²JKU, Solid state physics department, Linz, Austria — ³JKU, Institute of organic chemistry, Linz, Austria — ⁴University of Paderborn, Physik department, Paderborn, Germany

In our work we present the first X-ray spectroscopic investigation of free base 5,10,15-tris(pentafluorophenyl)corrole (TPFC) and manganese 5,10,15-tris(pentafluorophenyl)corrole (MnTPFC) on the Ag(111) surface. Our study is based on X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy measurements and combined with density functional theory (DFT) simulations. For both species we characterized all relevant regions and edges. Our analysis indicates a mixed 3+/4+ state of the Mn inside the MnTPFC. Furthermore, polarization-dependent NEXAFS measurements indicate for both molecules a low degree of order in the multilayer. In contrast, the first monolayers in contact with the silver substrate adsorb highly ordered, with the tetrapyrrolic macrocycle almost parallel to the surface, the residual tilt being ca. 20°. The three pentafluorophenyl groups are tilted by ~45° with respect to the surface.

O 12.11 Mon 17:30 MA 005

Massive conformational changes during thermally induced self-metalation of 2H-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin on Cu(111) — MICHAEL STARK, STEFANIE DITZE, MICHAEL LEPPER, LIANG ZHANG, HANNAH SCHLOTT, FLORIAN BUCHNER, MICHAEL RÖCKERT, MIN CHEN, OLE LYTKEN, HANS-PETER STEINRÜCK, and ●HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

Based on a combined scanning tunneling microscopy and X-ray photoelectron spectroscopy study we present detailed insights into pronounced changes of long-range order and intramolecular conformation during the self-metalation of 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) to CuTTBPP on Cu(111). 2HTTBPP adsorbed on Cu(111) at room temperature forms a peculiar entropically stabilized supramolecular ordered phase: the molecules arrange in alternating rows, with two distinct appearances in STM, which are assigned to concave and convex intramolecular conformations [1,2]. Upon metalation, the porphyrin literally “pops up” from the surface, due to a drastically reduced molecule-substrate interaction [3].

- [1] S. Ditze et. al, *JACS*, 136 (2014) 1609
- [2] H. Marbach, H.-P. Steinrück, *Chem. Commun.*, 50 (2014) 9034
- [3] M. Stark et al., *Chem. Commun.*, 50 (2014) 10225

O 12.12 Mon 17:45 MA 005

Engineering of large-pore metal coordination networks from de-novo synthesized porphyrins — ●YUANQIN HE¹, FELIX BISCHOFF¹, KNUD SEUFERT¹, WILLI AUWÄRTER¹, DAPHNE STASSEN², DAVIDE BONIFAZI², and JOHANNES BARTH¹ — ¹Physik Department E20, Technische Universität München, James Frank Str. 1, D-85748 Garching, Germany — ²Department of Chemistry and Namur Research College, University of Namur, Belgium

Molecular self-assembly using designed building blocks is a versatile method to fabricate nanostructures with tunable properties, wherein intermolecular interaction is a key factor that determines the structure. Here we present a low-temperature STM study on the self-assemblies of two differently substituted porphyrin species on Ag(111), namely (5,10,15,20)tetra-biphenylcyano porphyrin (2H-TPCN) and (5,10,15,20)tetra-pyridylphenylporphyrin (2H-TPyPP). Their distinct terminal substituents and the coordination to metal atoms, when adding Cu adatoms, induce different organic and metal-organic patterns. This allows us to explore the influence of the intermolecular interactions on the self-assembly and the formation of metal-organic coordination networks. Furthermore Monte-Carlo simulations are performed for these two systems, perfectly reproducing all the patterns observed in the experiment. The experimental results in combination

with the phase transition diagram derived from the simulation can give us a hint on the ratio between the coordination bond and vdW force, which can be further used to design molecular building blocks and self-assembly protocols.

O 12.13 Mon 18:00 MA 005

Impact of the bonding motif on the chirality transfer of DiOH[6]Helicene — •THOMAS NIJS¹, DAVID SCHWEINFURTH², ANELIA WÄCKERLIN¹, AISHA AHSAN¹, SYLWIA NOWAKOWSKA¹, FRANÇOIS DIEDERICH², CARLO THILGEN², and THOMAS A. JUNG^{1,3} — ¹University of Basel, Switzerland — ²ETH Zurich, Switzerland — ³Paul Scherrer Institute, Switzerland

Chirality plays an important role in biological processes as it generally affects molecular recognition by shape or geometry. Therefore, it needs to be crucially controlled, for example in pharmaceutical applications.

In order to address the impact of the intermolecular bonds and their strength on the chirality transfer [1], we employ an intrinsically chiral hexahelicene with two hydroxylic functional units [2]. We study the self-assembly at Ag(111) surface at sub-monolayer coverages under the regime of two different bonding motifs: H-bonding and metal-coordination. During deposition onto Ag(111) partial dehydrogenation occurs and H-bonded trimers are formed with a distinct chiral arrangement. By annealing in presence of Co adatoms added to the sample by sublimation, full dehydrogenation occurs and metal coordination bonds are established - while maintaining a trimeric motif. Importantly however, the system emerges into a new self-assembly pattern of the opposite chirality. The morphology of the self-assembly is investigated by STM and the bonding motif is investigated by surface chemical analysis i.e. XPS.

[1] A. Shchyrba et al., JACS, 135, 15270-15273 (2013)

[2] T. Nijs et al., manuscript in preparation