O 64: Organic Molecules on Inorganic Substrates IV: Adsorption, Growth and Networks

Time: Wednesday 10:30–13:45 Location: TRE Phy

O 64.1 Wed 10:30 TRE Phy

Interactions in STM-assembled molecular clusters — •Andreas Christ, Markus Leisegang, and Matthias Bode — Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The adsorption of organic molecules on metal surfaces has recently been studied intensive due to their potential application in electronic devices. For coverages up to a monolayer various self-assembled structures, including one-dimensional chains, Kagome lattices, or two-dimensional networks have been observed [1], which evolve from the delicate interplay of intermolecular and molecule-substrate interactions. To investigate these interactions more systematically, we employed STM manipulation of individual phthalocyanine molecules to manufacture molecular clusters and chains which vary in size and geometry. We observe that the tautomerization behavior of a single deprotonated phthalocyanine molecule changes as neighboring molecules are brought in close proximity. By changing the intermolecular distance and relative orientation we find that the tautomerization can be made asymmetric or hindered completely.

[1] Y. Wang *et al.*, AIP Advances **2**, 041402 (2012)

O 64.2 Wed 10:45 TRE Phy

Conformation controls mobility: 2H-Tetranaphthylporphyrins on Cu(111) — •Jan Kuliga[1], Stephen Masicot[1], Rajan Adhikari[1], Michael Ruppel[2], Norbert Jux[2], Hans-Peter Steinrück[1], and Hubertus Marbach[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — [2]Lehrstuhl für Organische Chemie II, Universität Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen, Germany

The adsorption behavior and the mobility of 2H-Tetranaphtylporphyrin (2HTNP) on Cu(111) was investigated by scanning tunneling microscopy (STM) at room temperature (RT). The molecules adsorb in the *inverted* structure, like the structurally related 2HTPP, with the naphthyl plane restricted to an orientation parallel to the Cu surface. The orientation of the four naphthyl groups yields altogether 16 possible conformations. Due to the existence of rotamer pairs, 10 different appearances are expected on the surface, which could all be identified by STM at RT. Most interestingly, the orientation of the naphthyl groups significantly influences the diffusion behavior of the molecules on Cu(111). We could identify three different groups of conformers, which are either immobile, medium or fast diffusing at RT. The mobility seem to decrease with increasing size of the footprint of the conformers on the surface.

O 64.3 Wed 11:00 TRE Phy

Quantitative confirmation of the inverted adsorption structure for 2H-tetraphenyl porphyrin on Cu(111) — Paul T. P. Ryan[1,2], Paula L. Lalaguna[1,3], Felix Haag[4], Mona M. Braim[5], Pencheng Ding[5,6], David J. Payne[2], Johannes V. Barth[4], Tien-Lin Lee[1], D. Phil Woodruff[5], Francesco Allegretti[4], and •David A. Duncan[1] — [1]Diamond Light Source, Didcot, UK — [2]Imperial College London, UK — [3]University of Glasgow, UK — [4]Technical University of Munich, Germany — [5]University of Warwick, Coventry, UK — [6]Harbin Institute of Technology, China

The inverted model has been proposed as the adsorption structure for tetraphenyl porphyrin (2H-TPP) on Cu(111) in recent publications[1,2]. In this model two of the 2H-TPP pyrrole rings are tilted almost perpendicular to the surface, moving the iminic N atoms into a surface bridge site and breaking the aromaticity of the porphyrin macrocycle. Published X-ray standing waves (XSW) data [3] was used to justify this model, yet that study was dogged by radiation damage and did not probe the lateral adsorption site of the molecule. Here we present a XSW study without such damage, addressing the lateral adsorption site of the iminic N atoms. These atoms are indeed found to occupy bridge or near-bridge adsorption sites on the surface, displaced laterally by 1.1 ± 0.2Åfrom direct atop sites. This result is in excellent agreement with the predicted value for these parameters in the inverted model, from the DFT calculations of Lepper et al., of 1.18 Å. [1] Chem. Comm. 53, 8207 (2017); [2] Chem. Mater. 31, 3009 (2019); [3] J. Phys. Chem. C 118, 13659 (2014)

O 64.4 Wed 11:15 TRE Phy

Arrangement and electronic properties of cobalt phthalocyanine molecules on Si(111) $(\sqrt{3}\times\sqrt{3})$ R30°-B — •Milan Kubicki, Martin Franz, Susi Lindner, Holger Eisele, and Mario Dähne — Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany

The formation of self-assembled monolayers of organic molecular materials on solid surfaces is an important subject because of their possible application in advanced optical and electronic devices. Here, the molecular arrangement and the interfacial electronic properties of cobalt phthalocyanine (CoPc) on the deactivated Si(111) $(\sqrt{3}\times\sqrt{3})$ R30°-B surface are studied by scanning tunneling microscopy and spectroscopy [1]. It is found that for submonolayer coverages the CoPc molecules lie flat on the Si surface with the Co d_{z^2} orbital of the molecule forming a hybrid state with the p_z orbital of the Si adatom at the surface. For multilayer coverages, in contrast, the CoPc molecules are tilted with respect to the Si surface forming highly ordered organic molecular films, and the electronic properties resemble those of pure CoPc.

[1] S. Lindner, M. Franz, M. Kubicki, S. Appelfeller, M. Dähne, and H. Eisele, Phys. Rev. B, in print (2019).

O 64.5 Wed 11:30 TRE Phy

Wetting of Porphyrin Multilayers on Rutile TiO2(110) — •Elmar Kataev[1], Daniel Wechsler[1], Federico Williams[2], Julia Köbl[1], Natalia Tsud[3], Kevin Prince[4], Hans-Peter Steinrück[1], and Ole Lytken[1] — [1]Friedrich-Alexander University Erlangen-Nürnberg, 91058, Erlangen, — [2]Universidad de Buenos Aires, Buenos Aires C1428EHA, Argentina — [3]Charles University, 116 36, Prague, Czech Republic — [4]Sincrotrone Trieste SCpA, Basovizza, Italy

Porphyrin/oxide hybrid materials find widespread applications in catalysis, sensors, organic electronics, and light-harvesting systems. However, molecular-level understanding of the interaction of porphyrins with oxides is missing. Here we report a photoemission study of the coverage- and temperature-dependent multilayer growth of cobalt(II) 5-monocarboxyphenyl-10,15,20-triphenylporphyrins (CoMCTPP) and cobalt(II) tetraphenylporphyrins (CoTPP) on a TiO2(110) surface. We find that CoTPP grows in layer-by-layer mode up to 3 layers, switching its behaviour to 3D growth afterwards. For CoMCTPP, we observe 3D growth directly after completion of the first layer. We describe this behavior by a roughness model consisting of a uniform film with sine-shaped islands on top of it. Subsequent annealing resulted in desorption without major rearrangement of the molecules. We conclude that a carboxylic group reduces the porphyrin mobility due to stronger molecular-substrate and molecular-molecular interactions. Supported by the DFG Research Unit FOR 1878 funCOS.

O 64.6 Wed 11:45 TRE Phy

Porous 2D networks formed by cyano-functionalized tetraphenyl porphyrins on Cu(111) — •Rajan Adhikari[1], Gretel Siglreithmaier[1], Jan Kuliga[1], Michael Lepper[1], Manuel Meusel[1], Helen Hölzel[2], Norbert Jux[2], Bernd Meyer[3], Hans-Peter Steinrück[1], and Hubertus Marbach[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr.3, 91058 Erlangen, Germany — [2]Lehrstuhl für Organische Chemie II, Universität Erlangen-Nürnberg, Nikolaus-Fiebiger-Str. 10 , 91058 Erlangen, Germany — [3]Computer-Chemistry-Center (CCC), Universität Erlangen-Nürnberg, Nägelsbachstr. 25, 91052, Erlangen, Germany

We investigated the adsorption of three related cyano-functionalized tetraphenyl porphyrin derivatives on Cu(111) by scanning tunneling microscopy in ultra-high vacuum with the goal to identify the role of the cyano group and the central Cu atom. The porphyrin derivatives studied were Cu-TCNPP, Cu-cisDCNPP, and 2H-cisDCNPP. Starting from different structures obtained after deposition at room temperature, all three molecules form the same long-range ordered hexagonal honeycomb-type structure with triangular pores, and three molecules per unit cell. For the metal-free 2H-cisDCNPP, this goes along with self-metalation. The structure-forming elements are pores with a distance of 3.1 nm, formed by triangles of porphyrins fused together by CN-Cu-NC interactions, with Cu adatoms. This finding leads us to suggest that the twofold cyano-functionalized at "cis" conformation is the minimum prerequisite to form a highly ordered 2D porous pattern.

O 64.7 Wed 12:00 TRE Phy

Heteromolecular bilayers on a weakly interacting substrate: Interactions and molecular distortions of F16CuPc — •Qi Wang[1], Antoni Franco-Cañellas[1], Jiacheng Yang[2], Julian Hausch[1], Samuel Struzek[1], Mengting Chen[2], Pardeep Kumar Thakur[3], Alexander Gerlach[1], Steffen Duhm[2], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — [2]Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, People's Republic of China — [3]Diamond Light Source, Harwell Science and Innovation Campus, OX11 0DE Oxfordshire, United Kingdom

Heteromolecular bilayers of π-conjugated organic molecules (COM) on metals, which are considered as model systems for more complex thin film heterostructures, are investigated with respect to their structural and electronic properties [1]. By exploring the influence of the organic-metal interaction strength in such bilayer systems, we determine the molecular arrangement in the physisorptive regime for copper-hexadecafluorophthalocyanine (F16CuPc) on Au(111) with template layers of 5,7,12,14-pentacenetetrone (P4O) and perylene-3,4,9,10-tetracarboxylic diimide (PTCDI). Using the X-ray standing wave (XSW) technique to distinguish the different molecular layers, we show that these two bilayers are ordered following their deposition sequence. Surprisingly, F16CuPc as the second layer within the heterostructures exhibits an inverted intramolecular distortion compared to its monolayer structure.

[1] Q. Wang, et. al., J. Phys. Chem. C. (2018) 122, 9480-9490.

O 64.8 Wed 12:15 TRE Phy

Tailoring adsorbed porphyrins with reactive metal centers — •Francesco Allegretti[1], David Duncan[1,2], Peter Deimel[1], Alissa Wiengarten[1], Willi Auwärter[1], Ari Seitsonen[3], and Johannes Barth[1] — [1]Physics Department E20, Technical University of Munich, Germany — [2]Diamond Light Source, Didcot, OX11 0DE, UK — [3]Département de Chimie, École Normale Supérieure, F-75005 Paris, France

Endowing adsorbed metal complexes such as porphyrins and phthalocyanines with specific functionalities can be of paramount importance for a range of applications, including heterogeneous catalysis, solar cells, and chemical sensors. The exploitation of on-surface reactions following the adsorption of free-base macrocyclic species on metal substrates provides an elegant route to tailor reactive centers in clean environments. Here, we report on the formation of Titanium(II) tetraphenylporphyrin (TiTPP) molecules on a Ag(111) surface by on-surface metalation. Unlike other metalloporphyrins we have previously studied, these species are very reactive even in the monolayer limit, and readily react with molecular oxygen to form oxotitanium porphyrin (TiOTPP) molecules with Titanium(IV) centers. We characterize the TiTPP and TiOTPP products at the molecular scale by a combination of X-ray spectroscopy, scanning probe microscopy and density functional theory to unravel details of the self-assembly, the molecular conformation and the oxidation state of the metal centers. Both molecules are promising candidates for future studies into model catalytic and photocatalytic reactions at surfaces.

Invited Talk O 64.9 Wed 12:30 TRE Phy

On-surface Chemical Reactions of Heterocycles for Functional Nanomaterials — •Shi-Xia Liu — Department of Chemistry and Biochemistry, University of Bern, Switzerland

On-surface chemical reactions are of high interest and have been intensively investigated in order to obtain carbon-based functional nanomaterials which very often can not be synthesized by wet chemistry. Thus, tailor-made heterocyclic precursors are becoming quite crucial in the development of highly symmetric 2D-conjugated porous architectures and N-doped graphene nanoribbons (GNRs) with desired functions due to their intrinsic electronic properties. This presentation focuses on our collaborative work on self-assembly and C-C coupling reactions on different surfaces leading to the formation of a range of nanostructures including small clusters,1 molecular wires,2 fully fused porphyrin-GNR hybrids3 and 2D-conjugated porous networks with Kagome characteristics.4 All these atomically precise nanostructures can be directly visualized by scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM). Their electronic properties can be fine-tuned by chemical modification and will be discussed.

References 1. N. Kocic et al., J. Am. Chem. Soc. 2016, 138, 5585-5593. 2. S. Karan et al., Angew. Chem. Int. Ed. 2019, submitted. 3. L. M. Mateo et al., Angew. Chem. Int. Ed. 2019, DOI: 10.1002/anie.201913024. 4. R. Pawlak et al., manuscript in preparation.

O 64.10 Wed 13:00 TRE Phy

On-surface Synthesis of Porphyrin-GNR Hybrid Chains — •Joel Deyerling[1], Mathias Pörtner[1], Luka Dordević[2], Alexander Riss[1], Davide Bonifazi[3], and Willi Auwärter[1] — [1]Physics Department E20, Technical University of Munich, Germany — [2]Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy — [3]School of Chemistry, Cardiff University, U.K.

In recent years, the on-surface formation of hybrid structures combining porphyrins and graphene nanoribbons (GNRs) attracted increasing interest [1-3]. A control on the precise atomic structure of such covalently linked porphyrin-based heterosystems is highly relevant for the tuning of their electronic and functional properties.

Here, we address dehalogenative coupling reactions of a bromonaphthalene functionalized Zn-porphyrin derivative on Ag(111) and Au(111). This precursor, its reaction steps, and different coupling motifs are characterized by scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) using a CO functionalized tip. Porphyrin-GNR hybrid chains exceeding a length of 20 nm are achieved. Our experiments reveal atomistic details of different coexisting coupling motifs, which holds great promise for future investigations of the corresponding electronic structure.

[1] J. Li *et al.*, Sci. Adv. 4, eaaq0582 (2018)
[2] L.M. Mateo *et al.*, Angew. Chem. Int. Ed., (2019)
[3] F. Bischoff *et al.*, Angew. Chem. Int. Ed., 57, 16030 (2018)

O 64.11 Wed 13:15 TRE Phy

Adsorption and intercalation of Zn porphines at the *h*-BN interface on Cu(111) — •Aleksandr Baklanov[1], David Duncan[2], Martin Schwarz[1], Knud Seufert[1], Johannes Küchle[1], Paul Ryan[2,3], Ignacio Piquero-Zulaica[1], Francesco Allegretti[1], and Willi Auwärter[1] — [1]Physics Department E20, Technical University of Munich, Germany — [2]Diamond Light Source, Harwell Science and Innovation Campus, Didcot, UK — [3]Department of Materials, Imperial College London, South Kensington, London, UK

Two-dimensional *h*-BN is an insulating layer used frequently to decouple adsorbed (metal-)organic molecules from the underlying metal single crystal support, thus preventing the strong influence of the latter on the molecular geometric and electronic properties [1,2]. The adsorption of Zn-porphine molecules on *h*-BN/Cu(111) as well as intercalation by placing the molecules between the *h*-BN cover and the Cu(111) [3], reveals distinct differences compared to porphine adsorption on bare Cu(111) [4]. Here we address the molecular conformation, adsorption structure, functionality of adsorbed and intercalated porphines, combined with the electronic and geometric structure of the *h*-BN by means of X-ray standing waves (XSW), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy/spectroscopy (STM/STS).

[1] W. Auwärter, Surf. Sci. Rep. **74**, 1 (2019).
[2] M. Schwarz et al., Nanoscale **10**, 21971 (2018).
[3] J. Ducke et al., ACS Nano **12**, 2677 (2018).
[4] M. Schwarz et al., J. Phys. Chem. C **122**, 5452 (2018).

O 64.12 Wed 13:30 TRE Phy

Ultrathin ionic liquid layers and organic molecules on metal surfaces — •Stephen Massicot, Matthias Lexow, Florian Maier, and Hans-Peter Steinrück — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Ionic liquids (ILs) are salts with melting points below 100°C and extreme low vapor pressure. Due to these properties, they have been studied extensively as promising candidates for various thin film applications, e.g in the fields of sensors, electrochemistry and catalysis. The interplay of ILs with organic molecules at metal surfaces in this context is highly important to understand and predict the behavior of these thin films applications.

In this study, we deposit ultrathin imidazolium IL layers and porphyrins by in-situ physical vapor deposition on a Ag(111) surface as model support. The structure and composition of the film at the solid and at the vacuum interface is studied by angle-resolved and temperature-programmed X-ray photoelectron spectroscopy on the molecular scale.

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