

O 19: Poster Session II: Organic molecules on inorganic substrates: Adsorption and growth II

Time: Monday 13:30–15:30

Location: P

O 19.1 Mon 13:30 P

Stereoselective cyclodehydrogenation of bishelicenes: preservation of handedness from helical to planar chirality

— BAHAAEDDIN IRZIQTAT^{1,2}, ●ALEKSANDRA CEBRAT^{1,2}, MILOŠ BALJOZOVIĆ¹, KEVIN MARTIN³, MANFRED PARSCHAU¹, NARCIS AVARVARI³, and KARL-HEINZ ERNST^{1,2,4} — ¹Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland — ²Department of Chemistry, University of Zurich, 8057 Zürich, Switzerland — ³Laboratoire Moltech-Anjou, CNRS-Université d'Angers, 49045 Angers, France — ⁴Nanosurf Laboratory, Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, Prague 6, Czechia

Here, we report the 2D chiral crystallization of 2,2'-bis(pentahelicene) on Au(111) and its thermal-induced dehydrogenation studied with scanning tunneling microscopy. The low coverage deposition on Au(111) kept at 400 K, leads to formation of heterochiral zigzag chains of the (M,M)- and (P,P)-enantiomers along the herringbone reconstruction pattern. In the closed-packed monolayer, both enantiomers self-assemble into racemic phase. Due to its strong sterical overcrowding in its adsorbate state, the (P,M)-meso form was not observed on the surface. Upon annealing and subsequent cooling of the substrate, the characteristic twisted shape of bis[5]helicenes can no longer be observed and only 2D homochiral conglomerate domains of planar Sp- and Rp-coronocoronene can be distinguished. The transformation from helical to planar chiral molecules via dehydrogenation and loss of eight hydrogen atoms was confirmed by secondary ion mass spectrometry.

O 19.2 Mon 13:30 P

Identifying Surface Adsorbate Structures with Bayesian Inference and Atomic Force Microscopy

— ●JARI JÄRVI, BENJAMIN ALLDRITT, ONDŘEJ KREJČÍ, MILICA TODOROVIĆ, PETER LILJEROTH, and PATRICK RINKE — Department of Applied Physics, Aalto University, P.O. Box 11100, 00076 Aalto, Espoo, Finland

Determining stable structures of organic molecular adsorbates on inorganic substrates requires both quantum mechanics and thorough exploration of the potential energy surface (PES). This is prohibitively expensive with density-functional theory (DFT). Bayesian Optimization Structure Search (BOSS) [1] is a new tool that combines DFT with Bayesian inference for accurate global structure search. BOSS applies strategic sampling to compute the complete PES with a small number of expensive DFT simulations. This allows a clear identification of stable structures and their energy barriers.

We apply BOSS to study the adsorption of (1S)-camphor on the Cu(111) surface as a function of molecular orientation and translations [2]. We identify 8 unique adsorbate types, in which camphor chemisorbs or physisorbs to the Cu(111) surface. We employ the most stable structures to produce simulated atomic force microscopy (AFM) images, which we use to identify adsorbate configurations in AFM experiments [3]. This study demonstrates the power of cross-disciplinary tools in detecting complex interface structures.

- [1] M. Todorović et al., *npj Comput. Mater.* 2019, 5, 35.
- [2] J. Järvi et al., *Beilstein J. Nanotechnol.* 2020, 11, 1577-1589.
- [3] J. Järvi et al., in preparation. doi:10.21203/rs.3.rs-50783/v1.

O 19.3 Mon 13:30 P

On-surface Synthesis of Porphyrin-GNR Hybrid Chains

— ●JOEL DEYERLING¹, MATHIAS PÖRTNER¹, LUKA DORDEVIC², ALEXANDER RISS¹, DAVIDE BONIFAZI³, and WILLI AUWÄRTER¹ — ¹Physics Department E20, Technical University of Munich, Germany — ²The School of Chemistry, Cardiff University, UK-CF10 3AT Cardiff, United Kingdom — ³Institute of Organic Chemistry, Faculty of Chemistry, University of Vienna, Austria

In recent years, the on-surface formation of hybrid structures combining porphyrins and graphene nanoribbons (GNRs) attracted increasing interest due to their potential for electronic, optoelectronic and spintronic applications [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) with CO functionalized tips. Porphyrin-GNR hybrid chains with lengths exceeding 20 nm are achieved. Our experiments reveal atomistic details of different coexisting coupling motifs and give first insights into the electronic structure of this porphyrin-GNR system.

- [1] J. Li et al., *Sci. Adv.* 4, eaaq0582 (2018)
- [2] L.M. Mateo et al., *Chem. Sci.* (2021)
- [3] F. Bischoff et al., *Angew. Chem. Int. Ed.*, 57, 16030 (2018)

O 19.4 Mon 13:30 P

Guiding molecular self-assembly by molecule-surface interaction

— OLE BUNJES¹, LUCAS A. PAUL², XINYUE DAI³, ●ALEXANDRA RITTMEIER¹, TOBIAS CLAUS¹, FENG DING³, INKE SIEWERT², and MARTIN WENDEROTH¹ — ¹IV. Physical Institute, University of Göttingen, Germany — ²Institute of Inorganic Chemistry, University of Göttingen, Germany — ³Ulsan National Institute of Science and Technology, Korea

One strategy for the generation of renewable fuels is the reduction of CO₂ to CO. Hence, the development of new hybrid systems catalyzing involved reaction steps is in the focus of current research. In this study the anchoring of the CO₂ reduction catalyst *fac*-Re(bpy)CO₃Cl (bpy = 2,2'-bipyridine) on the clean Ag(001) surface is investigated by means of scanning tunneling microscopy (STM) and density functional theory (DFT). Sub-monolayer films of the complex were deposited with the substrate held at 300K. STM measurements at 77K show that the beginning of cluster formation takes place at steps with a geometric orientation along the crystal axes <110>. The interaction between cluster and step leads to a restructuring of the surrounding step segments thereby promoting further cluster growth. Well-aligned decorated steps are found to be the nucleation point for higher dimensional growth. Comparing high resolution STM data to DFT calculations we get access to the local structural arrangement of the self-assembled complexes. Taking into account the calculated energies we develop a comprehensive growth model. This work was funded by the DFG - 217133147/SFB 1073, projects C1, C4, C7.

O 19.5 Mon 13:30 P

Surface-controlled reversal of the selectivity of halogen bonds

— JALMAR TSCHAKERT¹, QIGANG ZHONG¹, DANIEL MARTIN-JIMENEZ¹, JAIME CARRACEDO-COSME², CARLOS ROMERO MUNIZ², PASCAL HENKEL³, TOBIAS SCHLÖDER³, SEBASTIAN AHLES⁴, DOREEN MOLLENHAUER³, HERMANN A. WEGNER⁴, PABLO PUO², RUBEN PEREZ², ANDRE SCHIRMEISEN¹, and ●DANIEL EBELING¹ — ¹Institute of Applied Physics, Justus Liebig University Giessen, Germany — ²Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Spain — ³Institute of Physical Chemistry, Justus Liebig University Giessen, Germany — ⁴Institute of Organic Chemistry, Justus Liebig University Giessen, Germany

Halogen bonds are ideally suited for designing molecular assemblies because of their strong directionality and the possibility of tuning the interactions by using different types of halogens or molecular moieties. This is interesting for applications in supramolecular chemistry, crystal engineering, or drug design. Here, we present an approach for tuning the 2D self-assembly process of organic molecules by adsorption to reactive vs. inert metal surfaces. [1] Therewith, the order of halogen bond strengths that is known from gas phase or liquids can be reversed. Our approach relies on adjusting the molecular charge distribution, i.e., the σ -hole, by molecule-surface interactions. The polarizability of the halogen and the reactivity of the metal substrate are serving as control parameters. Our results establish the surface as a control knob for tuning molecular assemblies by reversing the selectivity of bonding sites. [1] Tschakert et al. *Nature Communications* 11, 5630 (2020)

O 19.6 Mon 13:30 P

Adsorption of organic molecules on the Cu(110)-(2x1)O stripe phase

— ●ILIAS GAZIZULLIN, CHRISTOPHE NACCI, and LEONHARD GRILL — Physical Chemistry Department, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria

The deposition of molecules onto single-crystal surfaces allows their investigation at the single-molecule level by scanning tunneling microscopy (STM), in particular for planar molecular structures. Here, we have studied flat dibromoanthracene (DBA) molecules on the

Cu(110)-(2x1)O stripe phase under ultra-high vacuum conditions with low-temperature STM. The Cu(110)-(2x1)O stripe phase is of particular interest since it offers alternating stripes of (metallic) Cu(110) areas and of oxygen-covered copper areas where the molecules are slightly decoupled from the metal substrate. The focus of our study is first on the preferred adsorption configuration and orientation of the linear molecules on the surface. It turns out that the molecules form organometallic chains on the copper areas, oriented in two surface directions. Second, we have attempted to investigate the electronic structure of the molecules by comparing their adsorption when they are on the metallic areas or on the oxide stripes. The results are compared with calculations of the molecular orbital structure.

O 19.7 Mon 13:30 P

Monodispersed graphene nanoribbons on Ag(111) by electro-spray controlled ion beam deposition: their self-assembly and on-surface extension visited by STM — ●WEI RAN¹, ANDREAS WALZ¹, KAROLINA STOIBER¹, PETER KNECHT¹, ANTHOULA C. PAPAGEORGIOU¹, ANNETTE HUETTIG¹, DIEGO CORTIZO-LACALLE², JUAN P. MORA-FUENTES², AURELIO MATEO-ALONSO^{2,3}, HARTMUT SCHLICHTING¹, JOACHIM REICHERT¹, and JOHANNES V. BARTH¹ — ¹Physics Department E20, Technical University of Munich, Germany — ²POLYMAT, University of the Basque Country UPV/EHU, Spain — ³Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Graphene nanoribbons (GNRs) are of interest due to their potential in electronics, energy conversion, and storage. For atomically precise GNRs, elaborate bottom-up fabrication protocols have been developed, utilising the reactivity of a metallic support. 1) However this approach often results in GNR arrays with a variety of lengths. Here we employ a different approach for the preparation and study of GNRs on surfaces: chemical synthesis and purification of well-defined nanoribbons 2) followed by processing with electro-spray controlled ion beam deposition (ES-CIBD). With this method, we can deposit well-defined GNRs on any solid support under ultra-high vacuum conditions. The quality of the films produced is exemplified for a 3 nm GNR on Ag(111). We explore their self-assembly and thermally activated polymerisation reactions by means of scanning tunnelling microscopy.

1) Fasel et al. Adv. Mater. 2016, 28, 6222. 2) Mateo-Alonso et al. Angew. Chem., Int. Ed. 2018, 57, 703.

O 19.8 Mon 13:30 P

Structural Details of a Prototypical Organic-Inorganic Interface: CuPc on In₂O₃(111) — ●MATTHIAS A. BLATNIK^{1,3}, PETER JACOBSON², MICHAEL SCHMID¹, JAN CECHAL³, ULRIKE DIEBOLD¹, and MARGARETA WAGNER¹ — ¹Institut f. Angew. Physik, TU Wien, Austria — ²School of Mathematics and Physics, University of Queens-

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Indium oxide (In₂O₃) is a ubiquitous material in OLEDs and photovoltaics due to an ideally matched optical transmission window and metal-like conductivity at room temperature when doped with Sn (as ITO). When In₂O₃ is paired with organic materials, a nearly universal fabrication step is the introduction of a thin organic buffer layer to improve the charge injection efficiency from In₂O₃ to the organic active layers. Using a combination of STM, nc-AFM and local spectroscopy (STS), we probe the adsorption structure and density of states (DOS) at the prototypical copper phthalocyanine (CuPc)-In₂O₃ interface. We focus on the stoichiometric (111) surface but also investigate the effects of dissociated water coadsorbed in UHV. STM/AFM imaging reveals single CuPc molecules adsorb in a flat, slightly tilted geometry in three symmetry-equivalent orientations. Increasing the coverage leads to (densely packed) 1D chains oriented along the <110> directions. With increasing coverage up to 1 ML, first a (2×2) and then a (1×1) superstructure is found. Finally, differential conductance (dI/dV) measurements reveal the energetic positions of the HOMO and LUMO states which are critical for improving charge injection.

O 19.9 Mon 13:30 P

Elucidating the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT — ●MARION VAN MIDDEN, MATIČ LOZINŠEK, TONE KOKALJ, and ERIK ZUPANIČ — Jožef Stefan Institute, Ljubljana, Slovenia

While organic corrosion inhibitors such as 2-mercaptobenzimidazole are widely used to protect the surface of copper, their bonding mechanism on the atomic scale remains elusive. DFT calculations have shown that different bonding configurations have comparable energies when considering the binding of a single molecule to the surface. In the case of larger coverages, which are common in real-life applications, various inter-molecular interactions have to be considered as well, further complicating calculations. To determine which interactions are most significant for the bonding and self-assembly of 2-mercaptobenzimidazole on the surface of Cu(111) we prepared samples in ultra high vacuum and imaged them using STM. Varying the evaporation rate and time as well as the substrate temperature allowed us to control the coverage and limit the energy the molecules have available to self assemble. Surprisingly the molecules formed ordered self-assembled structures even when depositing on samples cooled to approximately 50 K, which opposes the idea that strong binding to specific sites on the surface is crucial for corrosion prevention. The large variety of obtained self-assembled structures at different deposition parameters suggests, that the energy scales of competing interactions must be similar.