

## O 34: Poster Session III: Organic molecules on inorganic substrates: Adsorption and growth III

Time: Tuesday 10:30–12:30

Location: P

O 34.1 Tue 10:30 P

**Elucidating the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT** — ●MARION A. VAN MIDDEN, MATIC 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. These structures reassembled at temperatures below 100 K. Similarly, most of the observed structures rearranged when slightly heated. This 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.

O 34.2 Tue 10:30 P

**Comparison of the adsorptions of ethanol and azobenzene molecules on single-layer hexagonal boron nitride on Rh(111)** — ●KRISZTIÁN PALOTÁS<sup>1,2</sup>, ARNOLD FARKAS<sup>2,3</sup>, ÁDÁM SZITÁS<sup>2</sup>, DÁNIEL JURDI<sup>2</sup>, RICHÁRD GUBÓ<sup>2,3</sup>, TIBOR PÁSZTOR<sup>2</sup>, TIBOR AJTAI<sup>2,3</sup>, LÁSZLÓ ÓVÁRI<sup>2,3</sup>, JÁNOS KISS<sup>2</sup>, ANDRÁS BERKÓ<sup>2</sup>, and ZOLTÁN KÓNYA<sup>2</sup> — <sup>1</sup>Wigner Research Center for Physics, Budapest, Hungary — <sup>2</sup>University of Szeged, Szeged, Hungary — <sup>3</sup>ELI-ALPS, Szeged, Hungary

The nanomesh structure of single-layer hexagonal boron nitride (hBN) on various metal surfaces can be used as a nanotemplate for molecular adsorption. Possible applications can be molecular electronics, heterogeneous catalysis, sensing, or light harvesting. We investigate the adsorption properties of ethanol [1] and azobenzene [2] molecules on the hBN/Rh(111) surface by density functional theory calculations and experimental methods. We find high selectivity of the nanomesh structure for the azobenzene adsorption [2], but no selectivity for the ethanol adsorption [1]. The latter finding is in line with experimental observations of a very weak interaction between ethanol and the hBN/Rh(111) substrate [1]. Finally, we analyze the trans- and cis-azobenzene adsorption and azobenzene-azobenzene interactions in great details by using theoretical means [2]. These latter results contribute to the understanding of the behavior of photo-switching molecules on nanotemplated surfaces.

[1] A. P. Farkas et al. Appl. Catal. A: Gen. 592, 117440 (2020).

[2] Á. Sztás et al. J. Phys. Chem. C 124, 14182 (2020).

O 34.3 Tue 10:30 P

**Investigating kinetics of organic molecules on inorganic substrates** — ●ANNA WERKOVITS and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Growth processes of organic thin films are strongly influenced by the interplay of thermodynamics and kinetics. Following Ostwald's rule of stages, metastable structures often form first during the deposition process. Transitions to more stable structures may be prevented by fast aggregation and growth of the thermodynamically less stable seed, leading to a kinetically trapped polymorph. The selective growth of specific polymorphs, therefore, requires balancing growth and phase transitions via appropriately chosen deposition conditions.

The poster introduces a roadmap for achieving selective growth of organic-inorganic systems and gives an overview of the corresponding challenges and limitations. While thermodynamics can be sufficiently treated by now, kinetics are still an issue as reliable transition state searches devour computational resources. This is primarily caused by

the lack of suitable force fields and the high dimensionality of the potential energy surface. We provide first insights about the kinetics for the model system tetracyanoethylene (TCNE) on Cu(111). Energies are obtained using density functional theory (PBE+TS<sup>surf</sup>) and transition states mainly with the Nudged Elastic Band method.

O 34.4 Tue 10:30 P

**Computational Structure Prediction for Interfaces: What is Currently Possible?** — ●LUKAS HÖRMANN, ANDREAS JEINDL, FABIO CALCINELLI, JOHANNES CARTUS, and OLIVER HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Studying the electronic structure of organic monolayers on inorganic substrates requires knowledge about their atomistic structure. Such monolayers often display rich polymorphism arising from diverse molecular arrangements in different unit cells. The large number of arrangements poses a big challenge for determining the different polymorphs from first principles. To meet this challenge, we developed SAMPLE[1], which employs coarse-grained modeling and machine learning to efficiently map the minima of the potential energy surface of commensurate organic adlayers. With only a few hundred DFT calculations as input, we use Bayesian linear regression to determine the parameters of a physically motivated energy model. These parameters yield meaningful physical insight and allow predicting adsorption energies for millions of possible polymorphs with high accuracy. Beyond that, we continuously push the boundaries of surface structure search, with three noteworthy developments: i) predicting the second adlayer pursuing the goal of studying thin film properties; ii) generalizing SAMPLE to investigate incommensurate adlayers; iii) employing feature recognition to reveal hidden relationships between the interface properties. [1] Hörmann et al., Comput. Phys. Commun. 244, 143\*155, 2019

O 34.5 Tue 10:30 P

**On-surface synthesis of BN-doped carbon nanostructures** — ●TOBIAS WEISS<sup>1</sup>, ALEKSANDR BAKLANOV<sup>1</sup>, KNUD SEUFERT<sup>1</sup>, JOHANNES KÜCHLE<sup>1</sup>, MARC GONZALEZ CUXART<sup>1</sup>, FRANCESCO ALLEGRETTI<sup>1</sup>, JACOPO DOSSO<sup>2</sup>, DAVIDE BONIFAZI<sup>2,4</sup>, NICOLAS BACHELLIER<sup>3</sup>, MATTHIAS MUNTWILER<sup>3</sup>, and WILLI AUWÄRTER<sup>1</sup> — <sup>1</sup>Physics Department E20, Technical University of Munich, Germany — <sup>2</sup>School of Chemistry, Cardiff University, Cardiff, UK — <sup>3</sup>Paul Scherrer Institute, Villigen, Switzerland — <sup>4</sup>Institute of Organic Chemistry, Faculty of Chemistry, University of Vienna, Austria

Hybrid hexagonal boron nitride - carbon (BNC) layers provide promising properties for potential applications in electronics and gas adsorption [1]. Recently, BNC-based tectons were introduced to assemble covalent networks and supramolecular arrays on metal surfaces [1-3].

Here, we report the formation of BNC nanostructures on Ag(111) and Au(111) via bottom-up synthesis from borazine derivatives in UHV. We employed both a dehydrogenation approach using a BN-doped coronene derivative and an Ullmann-type coupling approach using a chlorine- and bromine-functionalized hexaphenylborazine. The resulting 2D structures, the sequential dehalogenation steps, and the Ullmann coupling are investigated with (fast) XPS and STM. Additionally, we probed the CO, CO<sub>2</sub>, and borazine adsorption on the BNC structures, revealing the inertness of the borazine core.

[1] M. M. Lorenzo-García et al., *Chimia*, 2017 **71**, 9, 550-557.

[2] C. Sánchez-Sánchez et al., *ACS Nano*, 2015 **9**, 9, 922.

[3] M. Schwarz et al., *Chem. Eur. J.*, 2018 **24**, 9565.

O 34.6 Tue 10:30 P

**Self-assembly and metalation of a novel macrocyclic biquinazoline compound on Ag(111)** — ●FELIX HAAG<sup>1</sup>, PETER S. DEIMEL<sup>1</sup>, PETER KNECHT<sup>1</sup>, RAPHAEL LAUENSTEIN<sup>2</sup>, MANUEL KASPAR<sup>2</sup>, KNUD SEUFERT<sup>1</sup>, YANG BAO<sup>1</sup>, MARC GONZALEZ CUXART<sup>1</sup>, ANTHOULA C. PAPAGEORGIOU<sup>1</sup>, CORINNA HESS<sup>2</sup>, WILLI AUWÄRTER<sup>1</sup>, JOHANNES V. BARTH<sup>1</sup>, and FRANCESCO ALLEGRETTI<sup>1</sup> — <sup>1</sup>Physics Department E20, Technical University Munich, Germany — <sup>2</sup>Chemistry Department, Technical University Munich, Germany

We report the first experimental study of the adsorption of the macrocyclic biquinazoline (H-Mabiq) compound on a model solid surface. Its two potential coordination sites for metal ions, combined with

multi-electron transfer capacity ensure higher sophistication beyond the well-studied metallo-porphyrins and -phthalocyanines. As the coordination sites can be occupied by different metal atoms, adsorbed Mabiq complexes are promising candidates for photocatalytic applications and epoxidation reactions. Here, we present the self-assembly, on-surface binding and chemical state of H-Mabiq on Ag(111) by employing a toolbox of surface science techniques including XPS, NEX-AFS, LEED, STM and TPD. We establish protocols for the preparation of well-ordered single layers and the controlled metalation with Co atoms. The ordering and packing of the pristine H-Mabiq single layer depend critically on the substrate temperature, evidenced through distinct changes in the LEED pattern and STM topography upon annealing. Moreover, the effect of Co deposition on the self-assembly and chemical state of the molecules is discussed.

O 34.7 Tue 10:30 P

**Asymmetric cyclotrimerization of terminal alkenes on Au(111)** — ●MIRUNALINI DEVARAJULU<sup>1</sup>, KEVIN DHAMO<sup>2</sup>, KONSTANTIN AMSHAROV<sup>3</sup>, BERND MEYER<sup>2</sup>, and SABINE MAIER<sup>1</sup> — <sup>1</sup>Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg — <sup>2</sup>Interdisciplinary Center for Molecular Materials (ICMM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander-Universität Erlangen-Nürnberg — <sup>3</sup>Institute for Chemistry, Martin Luther University of Halle-Wittenberg

Most branched, crosslinked, and networked polyphenylene polymers that have been assembled on metal surfaces *via* on-surface synthesis are non-conjugated because they contain metaphenylene units. In contrast, the on-surface synthesis of conjugated orthophenylene units remained so far elusive as rare by-products.

Here, we demonstrate the on-surface synthesis of conjugated 1,2,4-triphenylbenzenes *via* selective asymmetric cyclotrimerization of terminal alkenes on Au(111). We provide a detailed analysis of the reaction intermediates and final products *via* dehydrogenative homocoupling of terminal alkenes of linear 4-vinyl-1,1'-terphenyl molecules on Au(111) using low-temperature scanning tunneling microscopy in combination with density functional theory.

O 34.8 Tue 10:30 P

**Selective on-surface synthesis of oxygen heterocycles on metals**

— ●ANDREAS DÖRR<sup>1</sup>, NEMANJA KOCIĆ<sup>1</sup>, KONSTANTIN AMSHAROV<sup>2</sup>, and SABINE MAIER<sup>1</sup> — <sup>1</sup>Department for Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg — <sup>2</sup>Institute for Chemistry, Martin-Luther-Universität Halle-Wittenberg

Heterocycles with nitrogen, oxygen, or sulfur atoms are the basic units to incorporate chemical functionalization into carbon scaffolds. For oxygen-doped nanographenes, furan and pyran - having five- and six-membered rings, respectively - are the most common ones. However, their on-surface synthesis *via* cyclomerization reactions remains elusive so far. Here we present a low-temperature scanning tunneling microscopy study to understand the on-surface synthesis of furan and pyran derivatives from ketone-functionalized precursors on metal surfaces. We use thermally induced CH-activation reactions to fuse two ketone-derivatives in either *cis*- and *trans*-configuration selectively. Finally, cyclomerization reactions towards furan and pyran moieties are observed after further annealing. These results are highly unexpected because ketone derivatives are mostly known to convert to cyclic trimers or tetramers in solution-based chemistry. On the surface, however, the strong interaction of the ketones with the metal surface and adatoms opens up new reaction pathways.

O 34.9 Tue 10:30 P

**[n]Phenacene: Growth, Electronic Properties and On-Surface-Synthesis** — ●AKASH GUPTA<sup>1</sup>, PAUL YU-HSIANG YEN<sup>1</sup>, HSUAN TING LIN<sup>1</sup>, WUN CHANG PAN<sup>1</sup>, YONG-HE PAN<sup>1</sup>, GERMAR HOFFMAN<sup>1</sup>, and HIDEKI OKAMOTO<sup>2</sup> — <sup>1</sup>Department of Physics, National Tsing Hua University, Hsinchu, Taiwan — <sup>2</sup>Department of Chemistry, Okayama University, Japan

Chemical functionalization of solid surfaces and the study of respectively formed organic-metal interfaces from self-assembled molecular films to stacked layers attain a lot of attention. By means of an atomically precise design through a chemical approach, new materials and interfaces for organic electronics can be engineered. This offers a path to low cost, mechanically flexible, low weight components for organic electronics, such as OLEDs and OFETs through a chemistry driven bottom-up approach.

Pentacene, with a linear arrangement of five benzene rings, is intensively studied for prototype transistors but degrades under the presence of Oxygen. The chemically more robust [n]Phenacene, with n in a repeating W-shaped pattern fused benzene rings, was recently introduced as a promising alternative. Thereby, the electron mobility increases with n, the number of benzene rings.

Here, we study the growth and electronic properties of [10]Phenacenes on Au(111) and Ag(111) by Scanning Tunneling Microscopy/Spectroscopy at 77K and compare it to [5], [7], [9]Phenacene. The possibility of On-Surface-Synthesis of functionalized Phenacenes is discussed.