

## O 98: Organic-Inorganic Systems V: Adsorption on Metals

Time: Friday 10:30–13:15

Location: H24

O 98.1 Fri 10:30 H24

**Thiolate versus Selenolate: Structure, Stability, and Charge Transfer Properties** — •TOBIAS WÄCHTER<sup>1</sup>, JAKUB OSSOWSKI<sup>2</sup>, LAURA SILIES<sup>3</sup>, MARTIN KIND<sup>3</sup>, AGNIESZKA NOWOROLSKA<sup>2</sup>, FLORIAN BLOBNER<sup>4</sup>, DOMINIKA GNATEK<sup>2</sup>, JAKUB RYSZ<sup>2</sup>, MICHAEL BOLTE<sup>3</sup>, PETER FEULNER<sup>4</sup>, ANDREAS TERFORT<sup>3</sup>, PIOTR CYGANIK<sup>2</sup>, and MICHAEL ZHARNIKOV<sup>1</sup> — <sup>1</sup>Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany — <sup>2</sup>Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland — <sup>3</sup>Institut für Anorganische und Analytische Chemie, Universität Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt, Germany — <sup>4</sup>Physikdepartment E20, Technische Universität München, 85747 Garching, Germany

Self-assembled monolayers (SAMs) of 6-cyanonaphthalene-2-thiolate and -selenolate were prepared on Au(111) and characterized by several complementary spectroscopic techniques. The exact structural arrangements in both types of SAMs are somewhat different, but at the same time they have similar packing densities and molecular orientations. This permitted reliable competitive exchange and ion-beam-induced desorption experiments which provided unequivocal evidence for a stronger bonding of selenolates to the substrate as compared to the thiolates. Regardless of this difference, the dynamic charge transfer properties of both adsorbates were found to be nearly identical, as determined by the core-hole-clock approach, which is explained by a redistribution of electron density along the molecular framework, compensating the difference in the bond strength.

O 98.2 Fri 10:45 H24

**In-situ LEEM investigation of the growth of organic monolayers on metal surfaces** — •JANINA FELTER, CAROLINE HENNEKE, JANA WOLTERS, and CHRISTIAN KUMPF — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany, and Jülich Aachen Research Alliance (JARA)-Fundamentals of Future Information Technology, Germany

The adsorption of organic molecules on metal surfaces are of highest relevance for applications in the field of organic electronics and for fundamental studies of the interaction mechanisms. In particular, a deep understanding of the nucleation and the formation of the first molecular layer is necessary since this layer acts as a template for further growth and determines the electronic properties of the interface. By using LEEM, PEEM and  $\mu$ LEED, we studied the growth dynamics of Copper-II-phthalocyanine (CuPc) and 1,4,5,8-naphthalene-tetracarboxylic-acid dianhydride (NTCDA) monolayers on low-indexed metal surfaces in-situ and in real-time. Besides others, we have observed the transformation of CuPc domains into each other during and after deposition on Ag(111). In an ongoing PEEM-based ARPES study, we also investigate the electronic properties of these metal-organic interfaces.

O 98.3 Fri 11:00 H24

**Multiple molecular templates induced by dehydrogenation of a benzoquinone derivative on Cu(111)** — •GIUSEPPE MERCURIO<sup>1</sup>, NILS WIND<sup>1</sup>, SIMON WEISS<sup>2,3</sup>, SERGUEI SOUBATCH<sup>2,3</sup>, FRANK STEFAN TAUTZ<sup>2,3</sup>, and WILFRIED WURTH<sup>1,4</sup> — <sup>1</sup>Physics Department and Center for Free-Electron Laser Science, University of Hamburg, Hamburg, Germany — <sup>2</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Jülich, Germany — <sup>3</sup>JARA - Fundamentals of Future Information Technology, Germany — <sup>4</sup>DESY Photon Science, Hamburg, Germany

Organic layers on metal surfaces self-organize in a great variety of different surface templates depending on the intermolecular and molecule-metal interactions. The design of a molecular building block with specific structural and chemical properties needs to account for possible chemical modifications (e.g. dehydrogenation) upon deposition on a reactive substrate. In this context a fundamental understanding of the molecule/metal interface before and after dehydrogenation of the selected molecular unit is essential. To this end DHBQ (2,5-dihydroxyl-benzoquinone), a prototypical molecular building block for metal-organic networks, was investigated on the Cu(111) surface. It was found that the dehydrogenation of DHBQ can be thermally activated. Moreover, depending on the degree of dehydrogenation of the molecular layer different superstructures form on the surface. These

different molecular phases were investigated by means of x-ray photoemission spectroscopy, low-energy electron diffraction and normal incidence x-ray standing wave.

O 98.4 Fri 11:15 H24

**Structure formation of tetramantane[121] on copper(111)** — •MARVIN STIEFERMANN<sup>1</sup>, DANIEL EBELING<sup>1</sup>, PETER SCHREINER<sup>2</sup>, and ANDRÉ SCHRIMEISEN<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik der Justus-Liebig-Universität Gießen — <sup>2</sup>Institut für Organische Chemie der Justus-Liebig-Universität Gießen

Nanodiamonds are nanometer sized hydrocarbon molecules, which exhibit a diamondlike structure. As for other nanosized carbon materials (e.g. nanotubes or nanoribbons) diamondoids are discussed to exhibit tunable electronic properties[1]. For future applications in nanoelectronics it is therefore inevitable to study the interaction between diamondoids and solid substrates. Here, we studied the structure formation of tetramantane[121] on a close packed metal substrate with low temperature scanning tunneling microscopy. Tetramantane was evaporated at room temperature under UHV conditions onto a clean copper(111) surface using a self-constructed molecule gun. We observed that tetramantane forms islands on copper(111). Furthermore, we discovered different phases within these islands, which show commensurability with the substrate.

[1] Adhikari et al, Nanotechnology, Volume 26, Number 3, 035701,(2015)

O 98.5 Fri 11:30 H24

**On the Temperature-dependent Behavior of Ultrathin Ethylene Carbonate Films on Graphite(0001)** — •MARAL BOZORGCHENANI<sup>1</sup>, FLORIAN BUCHNER<sup>2</sup>, and R. JÜRGEN BEHM<sup>1,2</sup> — <sup>1</sup>Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — <sup>2</sup>Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

The interaction of ethylene carbonate (EC) with graphite(0001) as a model for the anode/electrolyte interface in Li-ion batteries was investigated under ultrahigh vacuum conditions. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIRS) were employed. After vapor deposition of a monolayer on graphite at 80 K the XP C1s and O1s spectra reveal the adsorption of intact adsorbed molecular adsorbates. Upon slow annealing the intensity of the XP signals related to EC drastically decreases in the temperature range between 190 and 210 K, mainly due to desorption. Subsequently, peaks with low intensity are still visible, which is related to decomposition products on the surface. FTIRS measurements at 80 K demonstrate modes of molecularly adsorbed EC. Difference spectra (background of the EC covered surface) recorded upon annealing reveal the evolution of bands with positive amplitudes (120 - 210 K) which are related either to molecular rearrangement effects or the formation of new species, and with negative amplitudes due to the loss of EC. At 210 K no EC is detected any more. The nature of the EC decomposition products is discussed and a comparison with our previous results on Cu(111) is given.

O 98.6 Fri 11:45 H24

**Carbene based molecular anchors on metal surfaces** — •BIBEK ADHIKARI<sup>1</sup>, SHENG MENG<sup>2</sup>, and MARIA FYTA<sup>1</sup> — <sup>1</sup>Institute for Computational Physics, Stuttgart, Germany — <sup>2</sup>Institute of Physics, Chinese Academy of Sciences, Beijing, China

N-hetero-cyclic carbenes (NHCs) are emerging as an alternative class of molecules to thiol-based self-assembled monolayers (SAMs). A carbon-gold bond is stronger than the sulfur-gold bond, making the carbene-based self-assembled monolayers much more stable in harsh environmental conditions. In this work, we have functionalized tiny hydrogenated diamond-like cages, known as diamondoids, using NHCs in order to prepare highly stable self assembled monolayers (SAMs) of diamondoids on metal substrates. Using quantum-mechanical simulations, we were able to extract the structural and electronic properties of the carbene-mediated diamondoid SAMs on metal surfaces. Two different configurations for the carbene-functionalized diamondoids are considered and attached on gold, silver, and platinum surfaces. The binding energy of S-Ag, S-Au, S-Pt and the comparison on the differences between thiol-metal and carbene-metal bonds are reported. A

preferential binding to platinum surfaces was found, while a modulation of the work function in all cases was clear. We mainly focus on the binding characteristics and stability of the NHC-mediated diamondoid SAMs. The surface morphology of all NHC-based diamondoid SAMs was shown through the simulated STM images which show characteristic features of each surface.

O 98.7 Fri 12:00 H24

**Beyond the hexagon: Non-alternant aromatic molecules on metal surfaces** — BENEDIKT P. KLEIN, PHILIPP MÜLLER, JOHANNA SCHEPP, FALK NIEFIND, MALTE ZUGERMEIER, MAIK SCHÖNINGER, MARTIN SCHMID, and ●J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Germany

The interaction of conjugated organic hydrocarbons, in particular aromatic species, with metal surfaces has been a major topic in surface science during the past decade. Up to now, the focus has been almost exclusively on alternant hydrocarbons, which are characterized by an even charge distribution and highly delocalized frontier orbitals. In contrast, non-alternant hydrocarbons have uneven charge distributions, which can result in considerable in-plane dipole moments, and more localized frontier orbitals. They also do not obey the Coulson-Rushbrooke pairing theorem and thus have shifted valence levels compared to the isomeric alternant hydrocarbons. In this contribution, we present the first systematic studies of non-alternant aromatic hydrocarbons on the (111) surfaces of Cu, Ag and Au. In particular, we focus on naphthalene as an alternant hydrocarbon and bicyclo[5.3.0]decapentaene (BDP) as its non-alternant counterpart. On the basis of extensive NEXAFS, PES, TPD and STM studies, we show that the non-alternant hydrocarbon interacts much stronger with the metal surfaces, especially in the case of Cu(111), and that the interaction is more localized. The non-alternant species also experiences a considerable out-of-plane deformation, which results from the localization of the frontier orbitals.

O 98.8 Fri 12:15 H24

**Layer-resolved evolution of perfluoropentacene thin films on Ag(110) surfaces** — ●EBRAHIM GHANBARI, MARKUS AIGLINGER, ANDREA NAVARRO-QUEZADA, THORSTEN WAGNER, and PETER ZEPPENFELD — Institute of Experimental Physics, Johannes Kepler University, Altenbergerstr. 69, 4040 Linz, Austria

The optical properties of organic thin films depend on the crystallographic structure and orientation. In addition, the interaction with the substrate can strongly affect electronic and optical properties. Here, we apply polarization dependent differential reflectance spectroscopy (pol-DRS) [1] and photoelectron emission microscopy (PEEM), simultaneously, to study the evolution of perfluoropentacene (PFP) thin films on Ag(110) surface. The adsorption of the organic molecules locally changes photoelectron emission yield of the surface giving rise to the contrast in PEEM. Therefore, PEEM is perfectly suited to study the evolution of the film morphology on the  $\mu\text{m}$  scale in real-time whereas, The pol-DRS is employed to investigate the temporal evolution of the (global) optical properties during thin film deposition. The variation of the PEEM and pol-DRS signals during PFP deposition reveal characteristic changes which can be attributed to the completion of subsequent layers and structural phase transition within these layers.

[1] A. Navarro-Quezada, M. Aiglinger, E. Ghanbari, Th. Wagner, and P. Zeppenfeld, *Rev. Sci. Inst.* 86, 113108 (2015)

O 98.9 Fri 12:30 H24

**A comparative STM study: adsorption behavior of different benzoporphyrin derivatives on coinage metals** — MICHAEL LEPPER, MICHAEL STARK, LIANG ZHANG, 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

A detailed comparative scanning tunneling microscopy (STM) study of

the self-assembly of different benzoporphyrin derivatives, among these Ni(II)-5,10,15,20-tetraphenyltetrabenzoporphyrin (NiTPBP) [1], the corresponding free-base analogue 2HTPBP and of Ni(II)-meso-tetrakis (4-tert-butylphenyl) benzoporphyrin (NiTTBPBP) [2], i.e., with additional tert-butyl groups at the para positions of the phenyl substituents on different substrates, namely Ag(111), Cu(111), Cu(110) and Cu(110)-(2x1)O will be presented and discussed. Depending on the actual molecule-substrate combination, the coverage and the sample temperature different adsorption behaviors are observed ranging from polymorphism [1], monomodal supramolecular arrangements [2] to the formation of molecular chains. The results will be interpreted based on the specific molecule-substrate and molecules-molecules interactions [1]. A particular focus will thereby be on the benzo groups which effectively establish a steric hindrance within the porphyrin macrocycle.

[1] M. Lepper et al., *J.Phys. Chem. C*, 119 (2015) 19897

[2] L. Zhang et al., *PCCP*, 17 (2015) 13066

O 98.10 Fri 12:45 H24

**Self-assembly of triphenylene molecules on the reconstructed Au(111) surface: influence of the surface stacking order** — SÖREN ZINT<sup>1</sup>, ●DANIEL EBELING<sup>1</sup>, SEBASTIAN AHLES<sup>2</sup>, HERMANN A. WEGNER<sup>2</sup>, and ANDRÉ SCHIRMEISEN<sup>1</sup> — <sup>1</sup>Institute of Applied Physics (IAP), Justus Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany — <sup>2</sup>Institute of Organic Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

Polycyclic aromatic hydrocarbons are an interesting component for the fabrication of nanoscale electronic devices, due to an extended pi-system and the possibility of forming graphene-like material. A powerful tool for the bottom-up fabrication of such nanostructures is molecular self-assembly. We study self-assembly of triphenylene molecules on the reconstructed Au(111) surface at submonolayer coverages by low temperature UHV STM at 5K. The molecules adsorb planarly, in two orientations only, corresponding to a 60° rotation. At low and medium coverages self-assembly is determined by strong attractive surface-molecule interactions and repulsive molecule-molecule interactions, which is accompanied by a one-to-one ratio of molecular orientations. At full monolayer coverage, however, the molecules undergo a reorientation into two different close-packed domains, leading to a significant overrepresentation of one molecular orientation. This reorientation strongly correlates with the stacking order of the substrate. Hence, the self-assembly process is controlled by the interaction of triphenylene with subsurface Au layers, which provides an additional mechanism for designing new systems.

O 98.11 Fri 13:00 H24

**Probing the Conformations of Synthetic Sequence Controlled Polymers** — IVAN PENTEGOV<sup>1</sup>, TAM TRINH<sup>2</sup>, ●STEPHAN RAUSCHENBACH<sup>1</sup>, UTA SCHLICKUM<sup>1</sup>, SABINE ABB<sup>1</sup>, LUDGER HARNAU<sup>1</sup>, SIMONE CONTI<sup>2</sup>, DUY LE<sup>3</sup>, TALAT RAHMAN<sup>3</sup>, MARCO CECCINI<sup>2</sup>, JEAN-FRANCOIS LUTZ<sup>2</sup>, and KLAUS KERN<sup>1</sup> — <sup>1</sup>Max-Planck-Institute for Solid State Research, Stuttgart — <sup>2</sup>Université de Strasbourg, France — <sup>3</sup>University of Central Florida, Orlando FL, USA

In natural as well as synthetic sequence controlled polymers (SCP) the sequence of building blocks covalently hardwires a secondary molecular structure, either to store information or to encode properties like molecular conformation. Therefore the two major challenges for the application of SCP are deciphering the sequence of a SCP and relating the sequence to its conformation. We employ scanning tunneling microscopy (STM) to characterize individual SCPs of the class of oligo-triazolamines (OTA) at highest spatial resolution. For this, electrospray ion beam deposition (ES-IBD) ensures chemical purity and intact deposition on ultrapure substrates. We observe conformations, which can be modeled by molecular dynamics (MD) simulations and density functional theory (DFT). Depending on the sequence, we find structural variety depending on the sequence of '0' and '1' represented by the absence or presence of a methyl group, respectively.