

O 77: Organic Molecules on Inorganic Substrates V: Solid-Liquid Interfaces, Self-Organization, Ordering

Time: Thursday 10:30–13:15

Location: H9

O 77.1 Thu 10:30 H9

Self-assembly of phospholipids on Au(111) as a model system for the cytoplasmic membrane — ●IRIS DORNER¹, ULRIKE DIEBOLD¹, GERHARD J SCHÜTZ¹, and STIJN F L MERTENS^{1,2} — ¹TU Vienna, Institute of Applied Physics, Wiedner Hauptstr. 8-10/134, 1040 Vienna, Austria — ²Lancaster University, Department of Chemistry, LA1 4YB, Lancaster, United Kingdom

Lateral organization of lipids and proteins plays a crucial role in biological processes such as cell signalling. In order to understand the interactions governing the organization of amphiphilic molecules, a model system must provide access to nanoscale information at the interface between a 2D-confined phase and liquid water. We present such a model system in the self-assembled monolayer and bilayer of phospholipids on Au(111). We study the stages of adsorption and the dynamics of our model system with complementary imaging techniques, electrochemical scanning tunnelling microscopy, atomic force microscopy and single-molecule fluorescence microscopy. These shed light on the initial adsorption mechanism via the monolayer, bilayer formation, as well as the much discussed formation of ordered lipid domains such as rafts.

O 77.2 Thu 10:45 H9

Controlling the surface adsorption of polyoxometalates from the liquid phase — ●MARIA GLÖSS^{1,2}, RICARDA PÜTT¹, MARCO MOORS², EMMANUEL KENTZINGER², WIM PYCKHOUT-HINTZEN², and KIRILL MONAKHOV³ — ¹RWTH Aachen — ²Forschungszentrum Jülich GmbH — ³Leibniz-Institute of Surface Engineering

Vanadium containing polyoxometalates (POMs) offer a wide range of potential applications due to their structural diversity appealing electronic properties. The probability of switching between multiple redox states without structural changes of the molecular system is one of the significant prerequisites for the development of molecule-based data storage devices.

For a technical implementation of POMs it is crucial to elucidate their adsorption behaviour on conductive substrates. In this study we investigate the droplet deposition from the liquid phase in order to correlate the molecular arrangement of POMs in solution and on weakly bonding surfaces.

Therefore, we characterise the adsorption behaviour of a functionalised Wells-Dawson-type POM on HOPG via STM and XPS. For the characterisation of the liquid phase SAXS is used. Depending on the water amount in the POM solution a complex agglomeration mechanism of the molecules is observed, which strongly affects the surface appearance after deposition resulting from defect-rich 2D molecular layers up to the formation of isolated metal-oxo cluster arrangements.

O 77.3 Thu 11:00 H9

Conformation control of peptides on surfaces via metal coordination — ●SABINE ABB¹, ELISE DUQUESNE², LUDGER HARNAU¹, STEPHAN RAUSCHENBACH^{1,3}, and KLAUS KERN^{1,4} — ¹Max Planck Institute for solid state research, Stuttgart, Germany — ²CNRS Paris, France — ³University of Oxford, UK — ⁴Ecole Polytechnique Fédérale de Lausanne, Switzerland

The conformation of peptides is defined by its sequence of amino acids and generally depends on the environmental conditions such as pH, salt concentration or temperature. Additionally, the coordination to metal centers can change the conformation, inducing also a change in the functionality of the peptide. Nearly half of all peptides/proteins are associated with metal coordination.

In this work, the metal-coordination complex is deposited by ES-IBD and investigated by STM. Here, we present the tailored conformation control of angiotensin-II (8 amino acids) on Au(111) by coordination to different metal centers. This is the first step towards rational design of surface supported peptide coordination complexes that can be relevant for different applications such as biomimetic catalysis.

O 77.4 Thu 11:15 H9

Specific Interactions of Organic Solvents on Hydrophobic Surfaces — ●ANNEMARIE PFNÜR¹, JOHANNES WILL², FLORIAN BERTRAM³, MILENA LIPPMANN³, and TOBIAS UNRUH¹ — ¹Institute of Crystallography and Structural Physics, Friedrich-

Alexander-Universität Erlangen-Nürnberg (FAU), Staudtstr. 3, 91058 Erlangen, Germany — ²Department of Materials Science and Engineering, Chair of Micro- and Nanostructure Research, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Cauerstr. 6, 91058 Erlangen, Germany — ³DESY Photon Science, Notkestr. 85, 22607 Hamburg, Germany

The stabilization mechanism of organic nanoparticles in aqueous dispersion produced by liquid antisolvent precipitation without additional stabilizers is under discussion. It is assumed that the solvent used in the production process forms a stabilizing layer at the interface of the nanoparticles.

In order to study this stabilizing layer, we developed a well defined planar model system for the liquid/solid interface. In a liquid cell, the interface of the sample to various solvents and solvent-water mixtures was studied by in-situ X-ray reflectometry (XRR).

A comprehensive analysis with a uniform model for all measurement curves demonstrated the existence of a solvent layer, with a thickness increasing systematically with the solvent concentration of the solvent-water mixture. The layer formation is correlated to the molecular size, the molar volume, as well as the polar and the hydrogen bond fraction of the Hansen solubility parameters.

O 77.5 Thu 11:30 H9

Molar Ratio of Building Blocks in Controlling the Domain Size of an Imine-Covalent Organic Framework — ●VIPIN MISHRA¹, VIVEK K YADAV², JAYANT K SINGH², and THIRUVANCHERIL G GOPAKUMAR¹ — ¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India — ²Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

Imine COF[1,2] (covalent organic framework) based on Schiff base reaction between p-phenylenediamine (PDA) and benzene-1,3,5-tricarboxaldehyde (TCA) is prepared on the HOPG-air interface. Using a combination of STM, AFM and XPS the microscopic formation of imine COF is confirmed. Role of the molar ratio of TCA and PDA has been explored and large smooth domains up to 2 μm are formed for high TCA ratio (> 2) compared to PDA. It is also observed that the quality of imine COF is strongly influenced by the presence of water atmosphere during the Schiff base reaction. The electronic property of imine COF is understood by experiment (tunneling spectroscopy) and dispersion corrected density functional theory (DFT) calculation. It is observed that the imine COF is semiconducting in nature with a band gap of ~1.9 eV. The calculation also indicates that the frontier orbitals are delocalized over the framework of imine COF. The calculated cohesive energy shows that the stability of imine COF is comparable to that of graphene.

[1] Y. Yu et al. Chem. Commun., 2016, 52, 8317. [2] X. Lirong et al. Angew. Chem. Int. Ed., 2014, 53, 9564.

O 77.6 Thu 11:45 H9

Structure of individual polythiophene molecules on Ag(111) — ●ERIK SCHRECK¹, STEFAN FÖRSTER¹, and WOLF WIDDRA^{1,2} — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

This talk presents a low-temperature scanning tunneling microscopy (STM) study of Poly(3-hexylthiophene) (P3HT) polymers on Ag(111). Submonolayer films were prepared by electrospray deposition under ultra-high vacuum conditions. Side chain resolved STM images reveal individual polymers and polymers forming condensed 2D structures. The distributions of end-to-end distance, radius of gyration and persistence length are derived by image analysis and are interpreted in terms of a 2D self-avoiding random walk.

In 2D condensates, we find enlarged persistence length and distinct bending angles between parallel polymer segments in comparison to isolated polymers. For the individual chains, the persistence length is smaller on Ag(111) than for Au(001)[2], which is discussed based on modified polymer-substrate interactions.

[1] S. Förster and W. Widdra, J. Chem. Phys. 141, 054713 (2014)
[2] S. Förster, E. Kohl, M. Ivanov, J. Gross, W. Widdra and W. Janke,

J. Chem. Phys. 141, 164701 (2014)

O 77.7 Thu 12:00 H9

Metalation and coordination reactions of 2H-meso-trans-di(p-cyanophenyl)porphyrin on Ag(111) with coadsorbed cobalt atoms — ●JAN KULIGA, LIANG ZHANG, MICHAEL LEPPER, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen

The controlled fabrication of functional molecular nanoarchitectures on surfaces is in the focus of our research activities. Thereby, we follow a bottom-up approach in which we rely on the adsorption behavior, i.e., self-assembly and in situ reactions of porphyrin derivatives as prototype functional molecules. In this context, we investigated the metalation and coordination reactions of Co with 5,15-bis(para-cyanophenyl)-10,20-bisphenylporphyrin (2HtransDCNPP) on a Ag(111) surface by scanning tunneling microscopy. At room temperature, 2HtransDCNPPs self-assemble into a well-ordered supramolecular structure stabilized by van der Waals interactions and intermolecular hydrogen bonding. The metalation to CotransDCNPP can be realized by pre- or post-deposition of Co atoms onto the Ag(111) surface. Interestingly, with *excess* Co material we observe the formation of peculiar structures appearing as 3 to 7 protrusion motifs in STM, with the dominating motif the 5-protrusion appearance.[1] The motifs could be identified through bias-dependent STM as 2 to 6 CotransDCNPPs coordinated by central Co atoms through peripheral cyano groups.

[1] Kuliga, et al., PCCP 20 (2018) 25062

O 77.8 Thu 12:15 H9

Auophilic interactions on surfaces — ●THORSTEN WAGNER¹, MICHAEL BRUNTHALER¹, MICHAEL GYÖRÖK¹, PETRA GRÜNDLINGER¹, UWE MONKOWIUS², and PETER ZEPPENFELD¹ — ¹Institute of Experimental Physics, Johannes Kepler University, Linz, Austria — ²School of Education, Johannes Kepler University, Linz, Austria

Metallophilicity describes attractive interactions between two or more metal atoms with closed shell configurations (i.e. d^8 , d^{10}). Metal complexes containing gold in the formal oxidation state +I exhibit a very strong interaction of this kind, which is often decisive for their arrangement in the solid state [1,2]. To study this auophilic interaction on surfaces, we prepared by physical vapor deposition films with a thickness of just a few layers of 2-naphthyl-isonitrile-gold(I)-chloride on Au(111) and Au(110) surfaces. The deposition was monitored by differential reflectance spectroscopy (DRS) and photoelectron emission microscopy (PEEM). After growth, the structure was characterized by means of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). In the case of the Au(111) substrate, we are able to confirm an anti-dimer structure similar to the bulk one demonstrating that the Au-Au interaction is preserved in the ultrathin films. For the Au(110) substrate, we did not observe the characteristic crossed swords arrangement [2]. In fact, the (1×2) reconstruction of the substrate surface is lifted upon adsorption of the molecules suggesting a sizable interaction between Au(I) complexes and Au substrate.

[1] P. Pyykkö, Chem. Rev. **97**, 597 (1997).

[2] E. Hobbollahi *et al.*, Inorg. Chem. Com. **65**, 24 (2016).

O 77.9 Thu 12:30 H9

Adsorption and Electronic Properties of N-Heteropolycyclic Molecules on Metal Surfaces — ●MOHSEN AJDARI¹, FRIEDRICH MAASS¹, MATTHIAS MÜLLER², CHRISTOPH HENDRICH², UWE H. F. BUNZ², A. STEPHEN K. HASHMI², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Universität Heidelberg — ²Organisch-Chemisches Institut, Universität Heidelberg

Small molecule organic semiconductors based on N-heteropolycyclic

aromatic compounds are promising candidates for a variety of (opto) electronic applications. In these molecules, introduction of nitrogen in their aromatic backbone in its pyridine form decreases the energy of both HOMO and LUMO, resulting in an improved stability due to an increased ionization potential and electron affinity of organic semiconductor, while the optical gap remains almost constant.

Understanding the adsorption and electronic properties of these molecules on inorganic substrates provides important insights into the charge transfer properties at organic/inorganic interface. High resolution electron energy loss spectroscopy (HREELS) is a powerful tool for investigating both the adsorption geometry via vibrational excitations and electronic properties of the molecules by utilizing electrons with sufficient energy to excite electronic transitions. In this study, HREELS is used to determine the adsorption and electronic properties of a new class of N-heteropolycyclic molecules as a function of coverage on Au(111).

O 77.10 Thu 12:45 H9

Formation of Si/organic interfaces using alkyne-functionalized cyclooctynes — CHRISTIAN LÄNGER¹, ●JULIAN HEEP¹, PAUL NIKODEMIAK², TAMAM BOHAMUD², PATRICK KIRSTEN¹, ULRICH HÖFER², ULRICH KOERT², and MICHAEL DÜRR¹ — ¹Justus-Liebig-Universität, 35392 Gießen — ²Philipps-Universität, 35037 Marburg

Controlled organic functionalization of semiconductor surfaces requires chemoselective adsorption of bifunctional molecules on the surface. Here we show for ethynyl-cyclopropyl-cyclooctyne (ECCO), an alkyne-functionalized cyclooctyne, that such chemoselective adsorption can be achieved on Si(001) despite the high reactivity of both functional groups in the molecule, i.e., the strained triple bond of cyclooctyne and the terminal triple bond. XPS and STM results clearly indicate that ECCO adsorbs selectively on Si(001) via a [2+2] cycloaddition of the strained triple bond without reaction of the ethynyl group. The latter can thus be used for further reactions and multilayer formation, e.g., by means of alkyne-azide coupling. The observed chemoselective reactivity of ECCO on Si(001) is traced back to the direct reaction channel of cyclooctyne [1] in contrast to the precursor-mediated adsorption pathway of the terminal triple bond.

[1] Reutzel et al., J. Phys. Chem. C **120** 26284 (2016).

O 77.11 Thu 13:00 H9

Phase diagram and order-disorder phase transitions of NTCDA/Ag(111) — ●SEBASTIAN THUSSING, MARTIN GRÜNEBOHM, and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, 35032 Marburg, Germany

A chopped-heating setup has been employed to derive the phase diagram and to follow order-disorder phase transitions of (sub-)monolayer NTCDA on Ag(111). This well-known model system has been chosen to optimize parameters in the experimental setup and to minimize detrimental effects associated with sample heating (direct current heating). We examined 2D SPA-LEED images taken at elevated temperatures as well as 1D line scans obtained during annealing of the molecular layers. NTCDA molecules on Ag(111) experience attractive lateral interactions, leading to island growth already at 150 - 200K for submonolayer coverages. Upon annealing the average NTCDA island size increases steadily (Ostwald ripening) as indicated by an increase of the correlation length of the relaxed monolayer NTCDA LEED reflexes. Further annealing eventually leads to a dissolution of NTCDA islands into the 2D gas phase. The temperature of this transformation depends strongly on the amount of deposited NTCDA. Moreover, this order-disorder transition is preceded by thermal desorption for coverages above 0.55 ML. By analyzing the coverage dependency of the order-disorder phase transition in conjunction with thermal desorption spectroscopy the phase diagram for this system has been derived.