

O 14: Organic, polymeric, biomolecular films – also with absorbates I

Time: Monday 15:00–16:45

Location: SCH A316

O 14.1 Mon 15:00 SCH A316

Reactive Adsorption effects on ordered Bis-terpyridine networks — ●THOMAS WALDMANN¹, DANIELA KÜNZEL², ACHIM BREITRUCK¹, HARRY E. HOSTER¹, AXEL GROSS², and R. JÜRGEN BEHM¹ — ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — ²Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

We tested the influence of H₂, O₂ and CO interaction with ordered networks of a Bis-terpyridine derivative (2,4'-BTP)[1,2] on Au(100), Ag(111) and Graphite (HOPG) surfaces using Video-STM (1 frame/s). Under UHV conditions[3,4] as well as in solution[1,2], the molecules form ordered networks on the single crystalline surfaces. Upon interaction with reactive gases, new structures are formed. The STM images are compared with DFT and MP2 calculations of the molecules in the gas phase.

[1] U.Ziener et al., Chem.Eur.J. 8, 951, 2002

[2] C. Meier et al., J.Phys.Chem.B 109, 21015, 2005

[3] H.E. Hoster et al., Langmuir 23, 11570, 2007

[4] M.Roos et al., Phys. Chem. Chem. Phys. 9, 5672, 2007

O 14.2 Mon 15:15 SCH A316

Stranski-Krastanov growth of Sexithiophene and para-sexiphenyl on Cu(110)-(2x1)O — ●LIDONG SUN¹, GÜNTHER WEIDLINGER¹, MARIELLA DENK¹, RICHARD DENK¹, MICHAEL HOHAGE¹, PETER ZEPPENFELD¹, STEPHEN BERKEBILE², GEORG KOLLER², FALKO.P. NETZER², and MICHAEL.G. RAMSEY² — ¹Institute of Experimental Physics, Johannes Kepler University Linz, Austria — ²Institute of Physics, Karl-Franzens University Graz, Austria

The initial stage of Sexithiophene (6T) and para-sexiphenyl (p-6P) growth on Cu(110)-(2x1)O has been investigated by in-situ reflectance difference spectroscopy (RDS) and scanning tunneling microscopy (STM). For both organic molecules, the optical response of the thin films shows a strong anisotropy indicates that the molecules are lying down on the surface with their long axis parallel to the [001] direction of the Cu(110) surface. Furthermore, the RD spectra of the growing films reveal systematic changes with increasing of film thickness reflecting a clear evolution of the absorption spectrum from a single molecule like to molecular crystal exciton. The observed evolution of the optical anisotropy also clearly shows that both 6T and p-6P thin films follow a Stranski-Krastanov growth mode with two ML thick wetting layers. Corresponding STM investigation on the morphology of 6T and p-6P thin films of up to two monolayers confirms the conclusion deduced from RDS results.

O 14.3 Mon 15:30 SCH A316

Experimental and theoretical NEXAFS investigations of metalloporphyrin films — ●NORMAN SCHMIDT¹, CHRISTIAN HUB¹, WOLFGANG HIERINGER², THOMAS STRUNSKUS³, and RAINER FINK¹ — ¹Univ. Erlangen, Physikalische Chemie II, Erlangen, Germany — ²Univ. Erlangen, Theoretische Chemie, Erlangen, Germany — ³C.-A.-Univ. Kiel, Lehrstuhl für Materialverbunde, Kiel, Germany

Metallo-porphyrins are well-known as electron donors in photoinduced electron transfer processes and for their semiconducting properties. They are used as, e.g., dyes, sensitizers, catalysts and in various organo-electronic devices. For improved device design and performance, more detailed knowledge about film morphology and related electronic structure is necessary. In the present study, the electronic structure of thick films of (H₂, Mn, Fe, Co, Zn, Sn)-tetraphenylporphyrins on Au-plated Si-wafers was investigated using NEXAFS spectroscopy. The obtained N 1s spectra reflect modifications in the electronic structure of the central metal ion interacting with the nitrogen donor functions of the porphyrin ring. Furthermore, the orientation of ultrathin and thick films of ZnTPP and SnTTBPP(OH)₂ (TTBPP=tetra(p-tert.butylphenyl)porphyrin) on an Ag(100) single crystal was studied by angle-dependent NEXAFS spectroscopy. In thin films, the porphyrin frame is lying almost flat on the surface, while the phenyl ligands are twisted by about 60 degrees with respect to the surface plane. Corroborating high-level TD-DFT calculations were used to allow more detailed interpretation of the experimental data (this project is funded by the DFG within SFB 583, TP C9).

O 14.4 Mon 15:45 SCH A316

Controlled formation of axially bonded Co-phthalocyanine dimers — XIN GE¹, CARLOS MANZANO¹, ●RICHARD BERNDT¹, LENNART T. ANGER², FELIX KÖHLER², and RAINER HERGES² — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, D-24098 Kiel — ²Otto Diels-Institut für Organische Chemie, Christian-Albrechts-Universität, D-24098 Kiel

STM is used to laterally move single Co-Phthalocyanine (CoPc) molecules on an ordered CoPc layer and to investigate the electronic states of the resulting structures. DFT calculations show that an axial Co-Co bond is formed from the d_{z²} orbitals when molecules are positioned almost vertically on top of each other. This leads to a substantial increase of the conductance of the molecular center at negative bias. The results demonstrate the critical importance of precisely controlling the molecular environment when investigating conductances. Moreover, the results show that axial bonding may be used to achieve three-dimensional molecular architectures on a surface and that STM can be used as a powerful tool to elucidate the nature of unusual chemical bonding modes. Financial support via SFB 677 is gratefully acknowledged.

O 14.5 Mon 16:00 SCH A316

The Effect of Different Substituents on the Surface Composition of Ionic Liquids - An ARXPS study (interchanged with O 14.6) — ●CLAUDIA KOLBECK¹, KEVIN ROBERT JOHN LOVELOCK¹, TILL CREMER¹, NATALIA PAAPE², PETER WASSERSCHIED^{2,3}, and HANS-PETER STEINRÜCK^{1,3} — ¹Lehrstuhl für Physikalische Chemie II, Egerlandstr. 3, 91058 Erlangen — ²Lehrstuhl für Chemische Reaktionstechnik, Egerlandstr. 3, 91058 Erlangen — ³Erlangen Catalysis Resource Center (ECRC)

A molecular understanding of ionic liquid (IL) surfaces is essential in order to explain related macroscopic properties such as surface tension. Due to their low vapour pressure ILs, i.e., molten salts with melting points below 100 °C, can be studied employing surface science techniques under ultra-high vacuum conditions. Angle resolved X-ray photoelectron spectroscopy (ARXPS) was used to investigate the change in surface composition of imidazolium based ionic liquids (ILs) by systematic variation of non-functionalised and functionalised groups attached to the molecules. For [C_nMIm][Tf₂N] (n = 2-16) with saturated carbon chains of different length as substituents of the imidazolium cation, a surface enrichment of the chains was clearly observed for n ≥ 4. Enrichment of the aliphatic carbon also occurs for alkyl groups attached to the anion as observed for [C₂MIm][C₈OSO₃].^[1] Poly(ethyleneglycol)ether functionalities introduced in the cation chain, however, lead to a stoichiometric surface composition, and, thus, to no enrichment of the chains.^[2]

[1] K. R. J. Lovelock et al., submitted to *J. Phys. Chem. B*.

[2] C. Kolbeck et al., *Langmuir* 2008, 24, 9500.

O 14.6 Mon 16:15 SCH A316

Surface Composition and Electronic Structure of Ionic Liquids - Influence of the anion (interchanged with O 14.5) — ●TILL CREMER¹, CLAUDIA KOLBECK¹, KEVIN ROBERT JOHN LOVELOCK¹, FLORIAN MAIER¹, NATALIA PAAPE², PETER STEFFEN SCHULZ², PETER WASSERSCHIED², and HANS-PETER STEINRÜCK¹ — ¹Lehrstuhl für Physikalische Chemie II, Egerlandstr. 3, 91058 Erlangen — ²Lehrstuhl für Chemische Reaktionstechnik, Egerlandstr. 3, 91058 Erlangen

Ionic Liquids (ILs) are a new class of solvents exhibiting unique physico-chemical properties. They are promising candidates for many applications in electrochemistry, synthesis, separation and lubrication technologies, and catalysis. For many of these processes knowledge of the interface, e.g. the IL-vacuum interface is of fundamental value. Due to their extremely low vapour pressure IL surfaces can be investigated under ultra high vacuum conditions such as X-ray photoelectron spectroscopy (XPS). In an extended angle resolved XPS (ARXPS) study, the near surface region of a wide range of 1-octyl-3-methylimidazolium based Ionic Liquids (ILs) was investigated. While for all IL surfaces enhancement of the alkyl chain was observed by ARXPS, the level of alkyl enhancement was found to be significantly dependent on the nature of the anion. Moreover, careful analysis of the fine structure of the C 1s region resulted in observation of an anion-dependent difference in relative binding energy positions for chemically different

carbon species present in the imidazolium cation. These shifts were compared and correlated to ^1H - and ^{13}C -NMR measurements. This work was supported by the DFG through SPP 1191 "Ionic Liquids".

O 14.7 Mon 16:30 SCH A316

In-situ EC-STM studies on the influence of halide anions on structure and reactivity of Dibenzylviologen on Cu(100)

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Copper has become a focus of research activities over the last two decades due to its use as interconnect material in microchip design. Nitrogen-containing cationic organic molecules have been studied as additives for the so-called copper damascene process. In the present investigation the structures and reactivity of a Dibenzylviologen (DBV)

layer adsorbed on a bromide-modified Cu(100) surface have been studied by in-situ electrochemical STM and will be compared to the results on the chloride-modified substrate and the related Diphenylviologen (DPV). N,N'-dibenzyl-4,4'-bipyridinium molecules (Dibenzylviologen, DBV) spontaneously adsorb on a halide-modified Cu(100)-surface, forming distinctive patterns, which have been characterized by in-situ Scanning Tunneling Microscopy. Depending on the adsorption potential a striped phase, a cavitated phase and an amorphous phase have been identified. Cyclic Voltammetry indicates that even more processes take place on the surface, because if the potential is decreased beyond a range of fully reversible processes, an irreversible surface phase formation is observed at -450 mV vs. RHE. This surface phase passivates the surface against adsorption of the dicationic phase, so the charge reversal of the interface in the outer Helmholtz layer seems to be reduced.