

O 37: Metal substrates: Adsorption of organic / bio molecules V

Time: Wednesday 15:00–17:30

Location: SCH A118

O 37.1 Wed 15:00 SCH A118

A new approach to probe molecular orientation in aromatic self-assembled monolayers — NIRMALYA BALLAV¹, BJÖRN SCHÜPBACH², OLE DETHLOFF², PETER FEULNER³, ANDREAS TERFORT^{2,4}, and MICHAEL ZHARNIKOV¹ — ¹Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — ²Department Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany — ³Physikdepartment E20, Technische Universität München, 85747 Garching, Germany — ⁴Institut für Anorganische u. Analytische Chemie, Goethe-Universität Frankfurt, 60438 Frankfurt, Germany

The emergence of new technologies has triggered significant interest in aromatic self-assembled monolayers (SAMs). Applications of these systems rely on a precise knowledge of their structure, which can be in particular studied by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. There are, however, principal constraints, which makes it impossible to get complete information on the molecular orientation in aromatic SAMs on the basis of the NEXAFS data. To avoid these constraints, we apply a new approach, attaching to the oligophenyl backbone a specific group (nitrile) with two mutually perpendicular molecular orbitals, which, due to the hybridization with the orbitals of the phenyl rings comprising the backbone, are oriented either perpendicular or parallel to the backbone plane. Analysis of the data suggests that that aromatic molecules in the respective SAMs on Au(111) substrate are not only tilted, but also noticeably twisted, with the exact twist angle depending on molecular architecture.

O 37.2 Wed 15:15 SCH A118

Adatom driven self-assembly of TAPP molecules on Cu(111) surface — JONAS BJÖRK¹, MATTHEW DYER¹, MANFRED MATENA², MEIKE STÖHR², THOMAS JUNG³, and MATS PERSSON¹ — ¹Surface Science Research Centre, University of Liverpool, Liverpool, United Kingdom — ²NCCR Nanoscale Science and Institute of Physics, University of Basel, Basel, Switzerland — ³Paul Scherrer Institute, Villigen, Switzerland

A combined density-functional theory (DFT) and scanning tunneling microscopy (STM) study of a self-assembled network of 1,3,8,10-tetraazaperopyrene (TAPP) molecules on Cu(111) is presented. The TAPP molecule, deposited on a Cu(111) surface at a temperature of 150°C, self-assembles in a porous network, commensurate with the underlying Cu substrate. Structural optimization with DFT shows that the system is stabilized by the presence of Cu adatoms in the network. STM experiments show a bright protrusion in the crossing between four molecules, dominating the images at a sample voltage of 3 V. Simulated STM images show that the bright protrusion is a signature of the presence of Cu adatoms. The electronic feature responsible for the bright protrusion is shown to come from the interaction between TAPP molecules and Cu adatoms, and does not depend upon the underlying Cu substrate.

O 37.3 Wed 15:30 SCH A118

Di-4-mercaptopyridine on Au(111): A Tunneling Microscopy and Spectroscopy Study — BERNDT KOSLOWSKI, ANNA TSCHETSCHETKIN, and PAUL ZIEMANN — Universität Ulm, Institut für Festkörperphysik, Albert-Einstein-Allee 11, D-89069 Ulm

We report on STM and STS measurements at low temperature of di-4-mercaptopyridine (di-4MPy) molecules adsorbed on Au(111). The di-4MPy is typically used as precursor for SAM deposition of 4MPy in an electrochemical cell. Here, the molecules were sublimated from a crucible onto the Au sample held at a temperature slightly below 0 °C. By STM, we find two distinct kinds of molecules at the Au surface: the first is small and similar to the appearance of 4MPy monomers, and the second appears much larger in topography and is attributed to di-4MPy. At step edges we find exclusively 4MPy which points to a catalytic activity of steps dissociating dimers. Within terraces, the di-4MPy form islands expelling the herringbone reconstruction of the Au substrate. The structure within islands is complicated and is most probably a $c(12 \times 8\sqrt{3})$ built from two enantiomeric unit meshes having a windmill structure composed of 5 or sometimes 6 molecules. We analyze the LUMO of di-4MPy by *z*-*V* spectroscopy, and we discuss the absorption geometry of the molecules.

O 37.4 Wed 15:45 SCH A118

Understanding Pd island formation on self assembled 4-mercaptopyridine monolayers on Au(111) — JOHN KEITH and TIMO JACOB — Institut für Elektrochemie, Universität Ulm, 89081 Ulm

Self-assembled monolayers (SAMs) on metallic substrates show great potential for applications such as molecular sensors or biological nanodevices. Efforts have been made to metallize small, aromatic SAMs such as 4-mercaptopyridine (4MP) on Au(111) through electrochemical deposition methods with Pd. However, these methods have not yet been successful due to formation of 2-dimensional islands exhibiting non-metallic character [1]. Motivated by this study, we investigated Pd adsorption and diffusion on a 4MP-SAM using periodic density functional theory [2]. For different Pd coverages, we calculated potential energy surfaces for adsorption and diffusion across the 4MP-SAM, allowing investigation of diffusion processes that explain how Pd islands form. Our studies clearly show Pd cannot diffuse on the clean 4MP-SAM surface. Rather, Pd atoms aggregate into regions above the Au surface and between 4MP monomers. When Pd diffuses across a surface where Pd is already pre-adsorbed, diffusion barriers are greatly reduced from the presence of small particles of Pd. This suggests diffusion and island formation require pre-deposited Pd on the SAM and that these islands are not strictly 2-dimensional.

[1] H.-G. Boyden, *et al.*, *Nature Mater.*, **5**, 394 (2006). [2] J. A. Keith, T. Jacob, *Nano Lett.*, submitted.

O 37.5 Wed 16:00 SCH A118

Magnetic adatoms confined in L-methionine biomolecular nanogratings: from atomic diffusion to adatom self-alignment — AGUSTIN SCHIFFRIN^{1,2}, JOACHIM REICHERT², WILLI AUWÄRTER², GESINE JAHNZ¹, YAN PENNEC¹, ALEXANDER WEBER-BARGIONI¹, VALERI S. STEPANYUK³, LARISSA NIEBERGALL³, PATRICK BRUNO^{3,4}, and JOHANNES V. BARTH² — ¹Chemistry Department, University of British Columbia, Vancouver, Canada — ²Physik Department, TU München, Germany — ³MPI für Mikrostrukturphysik, Halle, Germany — ⁴ESRF, Grenoble, France

We exploit the self-assembly properties of the L-methionine amino acid on Ag(111) to steer the one-dimensional ordering of cobalt and iron adatoms. Our low-temperature scanning tunneling microscopy observations reveal how the individual adatoms spontaneously self-align with a preferred ~ 25 Å next-neighbor spacing in the self-assembled biomolecular nanogratings. For Co strings the pertaining equilibrium statistics and dynamics were monitored to assess the underlying long-range interactions with their anisotropic energy landscape. The effect of the surface-state electron quantum confinement on the atomic self-alignment is revealed by scanning tunneling spectroscopy (STS) mapping and ab initio calculations. Also, the influence of this electronic quantum confinement on the LDOS Kondo signature of the magnetic Co adatoms is assessed with STS measurements.

[1] A. Schiffrin *et al.*, *Phys. Rev. B* **78**, 035424 (2008).

O 37.6 Wed 16:15 SCH A118

Formation of azobenzene containing self-assembled monolayers on gold monitored by optical second harmonic generation — FLORIAN VOGEL¹, MARIO MEIER², ULRICH SIEMELING², and FRANK TRÄGER¹ — ¹Institut für Physik and Center for Interdisciplinary Nanostructure Science and Technology – CINSaT, Universität Kassel, Kassel, Germany — ²Institut für Chemie and Center for Interdisciplinary Nanostructure Science and Technology – CINSaT, Universität Kassel, Kassel, Germany

The azobenzene derivative Bis[4-(phenylazo)phenyl]disulfide was synthesized and used for the preparation of self-assembled monolayers (SAM) on gold substrates. Azobenzene derivatives can be switched between their “cis” and “trans” isomers by irradiation with light. This molecular system, which is an ideal candidate for photoswitchable devices, represents the most widely studied system for SAMs bearing photoactive functional units.

The adsorption dynamics of the molecules have been investigated in situ and in real time by optical second harmonic generation (SHG). It has been shown that the adsorption of the molecules on the gold substrate can be well described by second order Langmuir kinetics.

Additional ellipsometric measurements have confirmed that, in fact,

a monolayer of the molecules has been formed. The thickness was determined to be (12 ± 1) Å. This is in good agreement with the theoretical value.

O 37.7 Wed 16:30 SCH A118

Structure and excitonic coupling in self-assembled monolayers of azobenzene-alkanethiols on gold — ●CORNELIUS GAHL¹, ROLAND SCHMIDT^{1,2}, DANIEL BRETE^{1,2}, ERIK MCNELLIS³, WOLFGANG FREYER¹, ROBERT CARLEY¹, KARSTEN REUTER³, and MARTIN WEINELT^{1,2} — ¹Max-Born-Institut, Max-Born-Str. 2a, 12489 Berlin, Germany — ²Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ³Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Self-assembled monolayers of azobenzene-functionalized alkanethiols have been investigated with respect to their geometric structure and optical properties by UV/Visible and near-edge X-ray absorption fine structure spectroscopy in combination with density-functional theory. By attaching a trifluoro-methyl endgroup to the chromophore both the molecular tilt and twist angle of the azobenzene moiety are determined. Based on this detailed structure analysis the energetic shifts observed in optical reflection spectroscopy can be qualitatively described within an extended dipole model. This substantiates sizeable excitonic coupling among the chromophores and elucidates why *trans* to *cis* isomerization of the azobenzene photoswitch is strongly suppressed in densely-packed self-assembled monolayers.

O 37.8 Wed 16:45 SCH A118

Theoretical investigation of the adsorption of dithiolates on Au surfaces — ●KATRIN TONIGOLD and AXEL GROSS — Institute for Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Thiolates are one of the most commonly used anchor groups of molecules that form self assembled monolayers (SAMs), as they yield stable monolayers because of the strong Au-S-interaction. An even higher stability should be expected if disulfide-containing anchor groups are used. Such groups are bigger than single thiolates and might lead to different structures on the surface that could be used as a new type of template for surface reactions.

In cooperation with experimentalists from the chair of Physical Chemistry I at the Ruhr-University Bochum, the adsorption of 1,2-dithiolan species and related α,γ -dithiolates has been investigated by means of DFT-GGA-calculations. In order to understand the molecule-surface interaction, the electronic structure of the most stable adsorption configurations at different coverages has been analyzed. Furthermore, the effect of different rest groups attached to disulfide-containing anchor groups has been examined. Weak van der Waals forces between these rests were taken into account via post-Hartree-Fock calculations of molecular pairs in the gas phase.

Additionally, as there are both experimental and calculational hints [1] that thiolate adsorption on Au can induce surface rearrangements, the influence of defects on the molecule-surface interaction has been considered.

[1] P. Maksymovych et al., Phys. Rev. Lett. **97**, 146103 (2006).

O 37.9 Wed 17:00 SCH A118

Influence of water on the structure of SAMs formed by mercaptopyridine and aminothiophenol on Au(111): a DFT study — ●JAN KUČERA and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm, Germany

Self-assembled monolayers (SAMs) of nitrogen containing aromatic thioliates on gold have been proposed as a fundamental element for nano-electronic devices. The formation of aromatic SAMs as well as the preparation of metal-SAM-metal contacts [1] usually occur in an aqueous environment. However, theoretical studies addressing the structure and stability of SAMs typically neglect the influence of the solvent. Hence the detailed influence of the aqueous environment on the geometric and electronic structure of SAMs remains unclear.

We have studied the effects of water on the structural and electronic properties of Au(111)/mercaptopyridine (MPy) and Au(111)/aminothiophenol (ATP) complexes by means of density functional theory calculations. The interaction of water with both the nitrogen- as well as with the sulfur-tail of MPy and ATP on Au(111) were examined. Water binds to the N-tails of SAM/Au complexes via the formation of hydrogen bonds [2], but its interaction with the S-tail is rather weak. The overall effect of water on the binding of the SAMs to the Au substrate is negligible, however, this is significantly changed when ions bound to the SAMs are considered.

[1] Mila Manolova et al., Adv. Mater., doi:10.1002/adma.200801634, in press.

[2] J. Kučera, A. Groß, Langmuir, doi:10.1021/la802368j, in press.

O 37.10 Wed 17:15 SCH A118

Scanning tunnelling microscopy study of 4'-nitro-1,1'-biphenyl-4-thiol self-assembled monolayers on Au(111) — ●HEIKO MUZIK, LAXMAN KANKATE, ANDREY TURCHANIN, and ARMIN GÖLZHÄUSER — Fakultät für Physik, Universität Bielefeld, 33615 Bielefeld

Self-assembled monolayers (SAMs) of 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) on gold is a useful system for applications in chemical nanolithography¹. Nanopatterning of NBPT SAMs by electrons or extreme UV radiation results in the formation of amino terminated cross-linked areas^{1,2}. This transformation can flexibly be utilized for the engineering of complex molecular assemblies on gold surfaces, as for instance protein chips³. Despite of many promising applications, the structure of NBPT SAMs has not been characterized in detail. Here we present the first scanning tunnelling microscope study of NBPT SAMs on the technologically relevant Au(111) surfaces. The samples were prepared in solution and by vapour deposition in vacuum. We show that the structure of NBPT SAMs exhibits a complex polymorphic behaviour which strongly depends on the temperature and preparation details. We also discuss the observed reconstruction of the gold substrate.

[1] A. Gözlhäuser et al, Adv. Mater. 13 (2001) 806.

[2] A. Turchanin et al, Small 3 (2007) 2114.

[3] A. Turchanin et al, Adv. Mater. 20 (2008) 471.