

O 16: Organic, Polymeric, and Biomolecular Films I

Time: Monday 14:15–17:30

Location: H42

O 16.1 Mon 14:15 H42

Molecular Chirality uncovered - Circular Dichroism of Adsorbed Chiral Molecules — •THORSTEN KAMPEN¹, PHILIPP MARTIN SCHMIDT¹, JEONG WON KIM², HUGO DIL¹, and KARSTEN HORN¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Nano-Surface Group, Korea Research Institute of Standards and Science, Daejeon, Korea

The chirality of molecules is an intrinsic structural property that has a huge impact upon biological and chemical reactions. However, the identification of the chiral nature of molecules in the adsorbed phase has been proven difficult. Here, we report on the characterization of adsorbed chiral molecules with respect to handedness and chemical composition using photoemission spectroscopy with circular polarized light. The emission from the carbon atoms in tartaric acid adsorbed on Cu(110) surfaces shows circular dichroism, and the asymmetry changes sign as a function of the emission angle. Changing the handedness of the molecule reverses the sign in the measured asymmetry. No asymmetry in the angular distribution is observed for the achiral meso-tartaric acid. Alanine and cysteine are two amino acids with the same next-neighbor environment of the chiral center, with cysteine containing an additional sulfur atom in the end group. This difference leads to different adsorption behavior and opposite optical activity. However, the circular dichroism in core-level photoemission is identical for both molecules.

The above mentioned results show that the angular dependent asymmetry is an absolute representation of the molecular chirality.

O 16.2 Mon 14:30 H42

Surface and Interface Properties of Chrysene on inert Substrates — •BENGT JAECKEL and BRUCE PARKINSON — Colorado State University; Department of Chemistry; 200 West Lake Street; Fort Collins, CO-80523/USA

The growth and electronic structure of chrysene thin films was studied on four different inert substrates (Au(111), Ag(111), HOPG and SnS₂) under ultra high vacuum (UHV) conditions. These substrates have hexagonal symmetry and lattice constants much smaller than the growing chrysene overlayer. A flat-lying chrysene molecule has a 2D or pseudo chirality and ordered surface structures can form ordered chiral domains, racemic 2D unit cells or disordered structures. Variable temperature scanning tunneling microscopy (VT-STM) was used to study the surface structure and ordering of the molecules while X-Ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were used to study the electronic properties of the interfaces.

O 16.3 Mon 14:45 H42

Electronic and geometric structure of F4TCNQ on Cu(111): A joint experimental and theoretical study — LORENZ ROMANER¹, ALEXANDER GERLACH², FRANK SCHREIBER², STEFFEN DUHM³, NORBERT KOCH³, GEROLD RANGGER⁴, GEORG HEIMEL⁴, JEAN-LUC BRÉDAS¹, and •EGBERT ZOJER¹ — ¹Institut für Festkörperphysik, Technische Universität Graz, A-8010 Graz, Austria — ²Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — ³Institut für Physik, Humboldt-Universität zu Berlin, D-12389 Berlin, Germany — ⁴School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, USA

The physical and chemical properties of organic/metal interfaces are of high interest for organic and molecular electronics. We present results of ultraviolet photoelectron spectroscopy (UPS) and X-ray standing wave (XSW) measurements for F4TCNQ adsorbed onto the copper (111) surface.

To gain insight into the nature of the interaction between the metal and the molecules, the interface was modeled by means of density functional theory band-structure calculations using the VASP code. The results provide an accurate description of charge donation from the -CN lone pairs to the metal and the back donation from the metal into the molecular LUMO. The molecules are strongly bent and display a transition from a quinoidal to a benzoic structure. From a real space analysis of the charge redistribution and the electrostatic properties of the layer the overall workfunction increase can be explained.

O 16.4 Mon 15:00 H42

Polymorphism of Porphyrin Molecules on Ag(111): and how to weave a rigid monolayer — •HUBERTUS MARBACH, FLORIAN BUCHNER, KARMEN COMANICI, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Egerlandstraße 3, D-91058 Erlangen, Germany

Organic molecules play a prominent role for the development of new materials and molecular devices. An important group of such molecules are porphyrins. Their versatility and distinct chemical and electronic properties make them promising candidates for tailored catalytic processes and as building blocks for nanoscaled electronic devices. In the present paper we focus on studying the molecular arrangements of Cobalt-5,10,15,20-Tetraphenylporphyrin (CoTPP) and Cobalt-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenyl*porphyrin (CoTTBPP) on an Ag(111) surface by means of scanning tunneling microscopy (STM) in ultra high vacuum. In the monolayer regime, ordered domains were found for both investigated porphyrins. Whereas the smaller CoTPP exhibits only one molecular arrangement (square order), for the larger CoTTBPP four clearly distinguishable phases (two hexagonal, one square and one herringbone) were observed. Submolecularly resolved STM images reveal that the different molecular arrangements go together with different conformations of the individual molecules. The herringbone structure was solely observed after a thermal treatment and consists of interwoven molecules, which makes this phase especially rigid.

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O 16.5 Mon 15:15 H42

Microscopic Identification of Different Porphyrin Species in Composite Layers — •FLORIAN BUCHNER, VERONIKA SCHWALD, KARMEN COMANICI, KEN FLECHTNER, SVEN SCHÖFFEL, THOMAS LUKASCZYK, MICHAEL GOTTFRIED, HUBERTUS MARBACH, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße, 3,

The self-assembly of organic molecules on single crystal surfaces is an approach towards the creation of novel materials with outstanding properties. Porphyrins represent a group of molecules, which are of great interest for various applications and also for basic science. In this study, composite films of different mixtures of the free-base 2H-5,10,15,20-Tetraphenylporphyrin (2HTPP) and Metallo-TPPs (namely FeTPP and CoTPP) were prepared on Ag (111), and imaged in UHV using scanning tunnelling microscopy (STM). A novel preparation method was applied by in-situ deposition of iron atoms onto the 2H-TPP monolayer. Microscopic evidence for the successful complexation of 2HTPP with Fe will be given [1]. This method is now also exploited to fabricate composite layers with 2HTPP, CoTPP and FeTPP. Depending on the bias voltage, the different molecules appear as protrusions or depressions, with changing shapes. Considering the different electronic configurations and additional UPS measurements, the different porphyrins can be identified.

[1] Buchner et al., ChemPhysChem (in press) This work has been funded by Sonderforschungsbereich 583

O 16.6 Mon 15:30 H42

Dynamics in ordered networks of adsorbed oligopyridine molecules — •HARRY HOSTER, MICHAEL ROOS, MATTHIAS ROOS, ACHIM BREITRUCK, and JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, Germany

Using time resolved scanning tunneling microscopy we have studied selected dynamic phenomena in adlayers of bis(terpyridine)derivatives BTP on HOPG, Au(111), and Ag(111) at around room temperature. While the mobility of single molecules is too high for a direct observation in this temperature region, it is possible to evaluate the mobility of island edges and domain boundaries of ordered two dimensional networks. This reveals important information about typical process rates in self assembly processes. The roles of molecule-molecule and molecule-substrate interactions, with a particular focus on anisotropy effects due to the shape of the molecules, are discussed.

O 16.7 Mon 15:45 H42

A structural and electronic phase transition at a metal-organic interface: The role of intermolecular interactions

— ●S. SOUBATCH¹, L. KILIAN², A. HAUSCHILD³, R. TEMIROV¹, A. SCHÖLL², A. BENDOUNAN², F. REINERT², F. S. TAUTZ¹, M. SOKOLOWSKI³, and E. UMBACH² — ¹International University Bremen (Jacobs University Bremen as of spring 2007), Bremen, Germany — ²Universität Würzburg, Würzburg, Germany — ³Universität Bonn, Bonn, Germany

For the organic semiconductor 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) adsorbed on the Ag(111) surface, it is found experimentally that molecules in the diluted and disordered phase, prepared at low temperatures, and the ordered commensurate monolayer phase are in significantly different adsorption states. This is deduced from comparison of their structural organization (LEED and STM), vertical bonding distances and intermolecular distortions (NIXSW), and the electronic properties (STS and UPS). The experimental data prove that the observed difference in properties of these two states is primarily caused by strong intermolecular interactions.

O 16.8 Mon 16:00 H42

A photooptical switch - azobenzene carrying alkanethiols on gold — DANIEL BRETE^{1,2}, WOLFGANG FREYER¹, CORNELIUS GAHL¹, SANJA KORICA^{1,2}, ●ROLAND SCHMIDT^{1,2}, and MARTIN WEINELT^{1,2} — ¹Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin — ²Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin

The photoisomeric switch azobenzene can be linked to gold surfaces by alkanethiols forming self-assembled monolayers (SAMs, Au-S-(CH₂)_n-O-C₆H₄-N-N-C₆H₅). Sufficient decoupling of the azobenzene group from the surface is thereby necessary to maintain its ability to photoisomerize. Using the core-hole-clock technique and Resonant-Raman-Auger Spectroscopy we prove that the decay of the N1s-LUMO excitation is independent of chain lengths down to n=3. The resonance lifetime of ≥ 20 fs falls in the timescale of trans-cis conformational photo-isomerization. Functionalizing the azobenzene entity with an electronerative CF₃ endgroup leads to a shift of the HOMO and HOMO-1 orbitals and modifies the oscillator strength of the corresponding transitions. This may be relevant for the switching process. All SAMs are well oriented with the azobenzene entity adopting the trans-isomerization. Admixture of alkanes to the layer does not affect the molecular orientation. NEXAFS spectra show clear indication for optical switching of the molecules upon optical excitation at 350 nm.

O 16.9 Mon 16:15 H42

DFT applied to functionalized Azobenzene: Towards a description of molecular switches on alkanethiol SAMs — ●ERIK MCNELLIS, VOLKER BLUM, PATRICK RINKE, and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195, Berlin

Molecules with a reversible and controllable binary property are a research topic of increasing relevance. Azobenzene (C₆H₅-N₂-C₆H₅) and its derivatives represent one class of such 'molecular switches', with a known cis-trans isomerization in solution. In surface mounted geometries, ligands may be used to decouple the switch from the solid surface. The ligand may itself be chosen with a particular functionality in mind: e.g., an alkanethiol chain adds self-assembly capability to the molecular switch.

We employ density-functional theory (DFT) and linear response time-dependent DFT to study the effect of such ligands and different non-polar or polar head groups (e.g. CF₃, CH₃) on the molecular geometry and the resonant excitation energies, discussing the results in the context of self-assembled monolayers (SAMs). Depending on the nature of the linker group (e.g. O, NH, CH₂) used to bind the alkane, as well as the employed head group, the excitation energies may be tuned by approximately 0.5 eV. The computed structural properties provide conceptual insights into steric effects and a possible orientational order of the molecular switches.

O 16.10 Mon 16:30 H42

Photothermal patterning of organic monolayers: Monolayers from fluorinated silanes and alkynes — ●BENJAMIN KLINGEBIEL, STEFFEN FRANZKA, NILS HARTMANN, and ECKART HASSELBRINK — Fachbereich Chemie, Universität Duisburg-Essen, Universitätsstraße 5, 45141 Essen

Organic monolayers offer great opportunities to modify the surface properties of solid substrates. Many advanced applications require patterned organic monolayers. Recently, we reported a simple photothermal procedure for patterning of alkylsiloxane monolayers grown on native silicon substrates [1]. A focused beam of an argon ion laser at a wavelength of 514 nm is used for rapid large-area patterning. De-

spite a laser spot diameter of about 2.5 microns line widths down to 200 nm are reached [1,2]. Here we present new results which focus on patterning of monolayers which are formed i) via coating of native silicon substrates in millimolar solutions of fluorinated silanes and ii) via hydrosilylation of H-terminated silicon substrates with long-chain alkynes. Similar to alkylsiloxane monolayers, these monolayers exhibit a high thermal and chemical stability. Hence, photothermal patterning, yields narrow lines with widths down to 300 nm and 400 nm, respectively. In order to determine the effective activation energies of the overall patterning process, the experimental data is analyzed considering a simple photothermal model.

[1] T. Balgar, S. Franzka, N. Hartmann, E. Hasselbrink, Langmuir 2004, 20, 3525 [2] D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, Nano Lett. 2006, 6, 2358

O 16.11 Mon 16:45 H42

Laser-assisted fabrication of nanostructured organic templates for the selective adsorption of gold nanoparticles into confined domains — ●NILS HARTMANN, DANIEL DAHLHAUS, STEFFEN FRANZKA, and ECKART HASSELBRINK — Fachbereich Chemie, Universitätsstr. 5, Universität Duisburg-Essen

A new laser-assisted procedure for the fabrication of nanostructured organic templates is reported. Octadecylsiloxane monolayers are grown on native Si(100) substrates. Subsequently these coatings are patterned using a focused beam of an argon ion laser. Local irradiation results in photothermal decomposition of the monolayers and provides a means for rapid large-area patterning with a lateral resolution significantly below the laser spot diameter [1]. In particular, at a spot diameter of about 2.5 microns, structures with a width below 100 nm are prepared. The patterned monolayers then are chemically functionalized via amination of the remaining hydrocarbon tails. The final chemical patterns represent functional templates which are suitable to direct the adsorption and self-assembly of nanoscopic components into micro- and nanostructured arrays [2]. In particular, citrate-coated gold nanoparticles with an average diameter of 16 nm are shown to self-assemble into one-dimensional arrangements, such as single chains.

1. T. Balgar, S. Franzka and N. Hartmann, Appl. Phys. A 82 (2006) 689.

2. D. Dahlhaus, S. Franzka, E. Hasselbrink and N. Hartmann, Nano Letters 6 (2006) 2358.

O 16.12 Mon 17:00 H42

Electrospray Ion Beam Vacuum Deposition of Organic Molecules and Inorganic Clusters — ●STEPHAN RAUSCHENBACH, NICHIA THONTASEN, NICOLA MALINOWSKI, and KLAUS KERN — Max-Planck-Institut for Solid State Research, Nanoscale Science Department, Heisenbergstr. 1, 70569 Stuttgart

Electrospray Ionization (ESI) is widely used as ionization technique for mass spectrometric applications in biology and organic chemistry, because of the unique destruction free ionization of even large biological molecules from solution.

In our experiment ESI is used to bring nonvolatile compounds into gas phase. An apparatus employing differential pumping, ion optical devices and time-of-flight mass analysis (TOF-MS) was constructed in order to deposit ions created by ESI under very controlled conditions on solid surface in ultra-high-vacuum (UHV). The samples can be analyzed ex-situ or in-situ by a variable temperature UHV-STM/AFM.

The technique is demonstrated by two examples: the deposition of clusters and the creation of monolayer films of organic salts. Various types of large inorganic clusters could be ionized and deposited. The layers of organic salts on the other hand were formed from small cluster ions of the type A⁺(AB)_n. AFM images show single or double molecular layers depending on the substrate. On the surface the molecules can diffuse and align along substrate features like step edges.

S. Rauschenbach, F. Stadler, E. Lunedei, N. Malinowski, S. Koltsov, G. Costantini, K. Kern, *Electrospray Ion Beam Deposition of Clusters and Biomolecules*, Small 4 (2006)

O 16.13 Mon 17:15 H42

Abnormal pinning of the Fermi and vacuum levels in monomolecular self-assembled films — HEEJOON AHN¹, JAMES WHITTEN¹, and ●MICHAEL ZHARNIKOV² — ¹Department of Chemistry, The University of Massachusetts Lowell, Lowell, MA 01854, USA — ²Angewandte Physikalische Chemie, Universität Heidelberg, D-69120 Heidelberg, Germany

Ultrathin organic monomolecular films, while electric insulators, are generally believed to be in electrical contact with a photoelectron

spectrometer when adsorbed on metal substrates due to electron tunnelling that results in alignment of the Fermi levels of the film and the spectrometer. We show, however, that this generally applicable model is incorrect for these systems and that energy level alignment in photoemission experiments occurs in a complex fashion, involving both vacuum and Fermi levels of the monomolecular film, conductive substrate, and the spectrometer. While the Fermi levels of the substrate and spectrometer are aligned, vacuum level instead of Fermi

level alignment occurs between the substrate and the SAM. As a result, the binding position of the photoemission peaks related to the monomolecular film is not only determined by its chemical identity, but also by changes in the work function of the substrate and film itself. This effect should certainly be taken into account in drawing conclusions from photoemission spectra of self-assembled organic films and adsorbate systems.