

O 51: Metal Substrates: Adsorption of Organic/Bio Molecules III

Time: Wednesday 15:15–18:30

Location: MA 041

O 51.1 Wed 15:15 MA 041

Molecular 2D Ordering of Viologens Under Non-Equilibrium Condition - an EC-STM Approach — •DUC THANH PHAM, KLAUS WANDEL, and PETER BROEKMANN — Institut f. Physikalische und Theoretische Chemie, Uni Bonn

The structural characterization of 1,1'-dibenzyl-4,4' bipyridinium molecules (dibenzyl-viologen, DBV), adsorbed on a chloride modified Cu(100) electrode is studied by means of Cyclic Voltammetry (CV) and ElectroChemical Scanning Tunneling Microscopy (EC-STM). All previous studies on this system started with the non-reactive adsorption of DBV²⁺ in the double layer regime resulting in the surface assisted organization of a cationic DBV²⁺ monolayer on top of the c(2x2) anionic chloride adlayer. However, within the electrode potential window ranging from E = -150 mV to E = -250 mV where the first reduction step from the di-cationic to the radical mono-cationic viologen form takes place, a "reactive" adsorption of viologen occurs. Preferred reaction products at the surface are metastable viologen dimer species with a viologen coverage of 0.077 ML. Once formed under kinetic control, this dimer phase exhibits an unusually high stability against changes of the potential. It can only be converted irreversibly into either the oxidized dicationic species or the more compact and thermodynamically favorable "polymeric" stacking phase of radical mono-cations by significantly more anodic or cathodic potentials sweeps, respectively.

O 51.2 Wed 15:30 MA 041

Ultra-thin films of α -sexithiophene on Au(001) at room and elevated temperature — •ANKE HÖFER, KLAUS DUNCKER, MARIO KIEL, SEBASTIAN WEDEKIND, RENÉ HAMMER, and WOLF WIDDRA — Institute of Physics, Martin-Luther-Universität Halle-Wittenberg

The rodlike, π -conjugated molecule α -sexithiophene (α -6T) is widely used in organic electronics, in which the performance of the devices strongly depends on molecular order. Ultra-thin films of α -6T on Au(001) have been studied by scanning tunneling microscopy (STM) in UHV. At room temperature in the monolayer regime two different highly ordered adsorption phases coexist which are related to quenching (phase D) and conservation (phase L) of the underlying substrate reconstruction. As the molecular structure of D is identical to one found on Ag(001), the other one is similar to that observed on Au(111) [1]. Both structures show different homochiral domains necessitating chiral self-recognition of the adsorbed molecules. Thermally induced both phases disappear at 400 K, whereas the transition of L is irreversible. In-situ observations at elevated temperatures from 410 K up to 630 K show the formation of a molecular network, which is interpreted as result of thiophene polymerization. The onset temperature of polymerization differs for the surface areas with quenched and conserved reconstruction.

[1] M. Kiel, K. Duncker, Ch. Hagendorf, W. Widdra, Phys. Rev. B 75, 195439 (2007)

O 51.3 Wed 15:45 MA 041

Formation of covalently bound chains from Dibromoterfluorene molecules on Au(111) — •LEIF LAFFERENTZ¹, HAO YU², STEFAN HECHT², and LEONHARD GRILL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — ²Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

Supramolecular structures formed by self-assembly on surfaces have attracted a lot of interest in the last years. While the formation of arrays relying on non-covalent bonds can yield structures of high complexity, they tend to be not very robust. For nanostructures of potential interest for future applications, a more rigid connection of the molecular building blocks is required.

Recently, it has been shown in our group that it is possible to form molecular networks of pre-designed architecture by directed covalent linking of porphyrin molecules [1]. We will present results on the versatility of this method using differently designed building blocks, namely Dibromoterfluorene (DBTF). Intact molecules are found on the Au(111) surface in characteristic arrays. Upon sufficient heating, these molecules become "activated" and are connected by covalent bonds to form long chains. The constructed macromolecules are characterized by scanning tunneling microscopy (STM). Furthermore, manipulation of the molecular chains by using the STM tip will be presented. [1] L.

Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, and S. Hecht, Nature Nanotech. 2, 687 (2007)

O 51.4 Wed 16:00 MA 041

Protection group controlled surface chemistry-organization and heat induced coupling of biphenyl derivatives on metal surfaces — •SERPIL BOZ¹, MEIKE STÖHR¹, UMUT SOYDANER², and MARCEL MAYOR² — ¹University of Basel, Department of Physics, Klingelbergstrasse, CH-4056 Basel, Switzerland. — ²University of Basel, Department of Chemistry, St. Johannisring 19, CH-4056 Basel, Switzerland

The development of scanning probe methods enabled the investigation of molecules on surfaces with impressive resolutions. The arrangement of the molecules in ordered patterns occurs because of a delicate balance between molecule - substrate and intermolecular interactions such as van der Waals interactions, H-bonding or dipolar coupling. A very appealing concept is to profit from the order of these pre-organized structures and to interlink the molecular building blocks to macromolecules. A prominent example for this is diacetylenes which have been polymerized on surfaces either by UV-light or with aid of the STM tip. Here we would like to present our new concept to control both, the molecular self-assembly and the subsequent intermolecular coupling reactivity by protection group chemistry. We studied a BOC protected biphenyl derivative which forms a parallel and a herringbone arrangement at room temperature on a Cu (111) surface. A second phase is observed after the sample is annealed at 196°C and covalently linked dimers by splitting off the BOC groups are formed. As a result of further annealing, individual cross-shaped polymeric structures are obtained.

O 51.5 Wed 16:15 MA 041

Thermally induced polymerization of molecules on surfaces — •MANFRED MATENA¹, JORGE LOBO-CHECA¹, MEIKE STÖHR¹, KATHRIN MÜLLER², THOMAS A. JUNG², TILL RIEHM³, and LUTZ H. GADE³ — ¹Departement Physik, Universität Basel, Switzerland — ²Paul-Scherrer-Institut, Villigen, Switzerland — ³Institut für Anorganische Chemie, Universität Heidelberg, Germany

By utilizing the concepts of supramolecular chemistry, impressive results for molecular self-assembly on surfaces have been presented. Mostly, non-covalent interactions like metal coordination, hydrogen bonding or dipolar coupling are exploited to create extended supramolecular patterns in variable dimensions. One common approach to influencing these structures relies mainly on the sophisticated design of the molecular functional groups. Thus it makes use of properties already inherent to the molecules. In our work we have chosen a different concept. A thermally-induced surface-assisted reaction was used to modify the endgroups of a perylene derivative (TAPP) and thereby, the molecular interactions are altered.

TAPP was found to form a closed-packed assembly on Cu(111), whereas the intermolecular interactions are based upon vdW-forces. After annealing at 150°C, a metal coordinated rectangular network is obtained which is commensurate to the underlying Cu surface. In this case the organic molecules coordinate to Cu atoms through the lone pairs of their nitrogen atoms. A second annealing step at temperatures >240°C modifies the molecule on the surface and leads to covalently linked polyaromatic chains.

O 51.6 Wed 16:30 MA 041

Molecular self-assembly on an ultrathin insulating film — •CHRISTIAN BOMBIS^{1,2}, NATALIYA KALASHNIK¹, WEI XU¹, ERIK LAEGSGAARD¹, FLEMMING BESENBACHER¹, and TROLLE LINDEROTH¹ — ¹Department of Physics and Astronomy, and iNANO, University of Aarhus, 8000 Aarhus C, Denmark — ²Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Molecular self-assembly of cyanuric acid (CA) and melamine (M) on an ultrathin NaCl film grown on Au(111) is investigated by means of STM. Since it was shown that an ultrathin insulating film of NaCl on a metallic substrate enables electrical decoupling of an adsorbed molecule from the conducting substrate, while still allowing imaging of the molecule with STM, this method gained increasing attention for reasons of practical interest. However, due to weak molecule-substrate interactions stabilization of the molecules on alkali halides is a challeng-

ing task. In the present study we present the preparation and growth of ultrathin NaCl films in submonolayer quantities on Au(111). CA and M were thermally evaporated on such a NaCl/Au(111) substrate held at room temperature. We were able to image ordered molecular islands at comparatively high temperatures between 120 and 180 K on top of the NaCl film, which are nucleated at NaCl step edges. As we could identify the same adsorption structures on the NaCl film as previously reported by Xu et al.* for CA and M on pure Au(111), we conclude that the stabilization of the molecules is facilitated by their ability to form complementary triple hydrogen bond motifs with a high intermolecular interaction strength. *small 2007, 3, No. 5, 854-858

O 51.7 Wed 16:45 MA 041

Scanning Tunneling Microscopy Study of Iron(II) Phthalocyanine Growth on Metal and Insulating Surfaces — ●ALESSANDRO SCARFATO^{1,2}, SHIH-HSIN CHANG¹, GERMAR HOFFMANN¹, and ROLAND WIESENDANGER¹ — ¹Institute of Applied Physics and Microstructure Research Center Hamburg, University of Hamburg, Jungiusstrasse 11, D-20355, Hamburg, Germany — ²Dipartimento di Fisica “E. R. Caianiello”, Università degli Studi di Salerno e CNR-INFM Laboratorio Regionale SUPERMAT, via Salvador Allende, I-84081 Baronissi (SA), Italy

The growth behavior of iron(II) phthalocyanine (FePc) molecules on Cu(111) and on NaCl/Cu(111) surfaces up to a coverage ~ 1.5 ML has been studied by a variable-temperature scanning tunneling microscope. Molecules have been deposited at room temperature to allow for surface diffusion. At low coverage (~ 0.5 ML) no tendency of self assembling was observed, while at high coverages (> 1 ML) the second layer molecules self-organize to form long-range domains in the alpha phase. In order to tune molecule-substrate interaction insulating NaCl layers are introduced. Adsorption of FePc molecules on NaCl shows site specificity, i.e. the Fe atom adsorbs on top of a Cl⁻ anion. We will discuss our results on the growth morphology in terms of molecule-molecule and molecule-substrate interactions in comparison with previous findings for FePc on Au(111).

O 51.8 Wed 17:00 MA 041

STM and STS on Ultrathin Organic Layers of Fluorinated Cobalt Phthalocyanine (F16CoPc) on Crystalline Substrates — ●MAHMOUD ABDEL-HAFIEZ, MARIUS TOADER, THIRUVANCHERIL GOPAKUMAR, and MICHAEL HIETSCHOLD — Institute of Physics, Solid Surfaces Analysis Group, Chemnitz University of Technology, D-09107, Chemnitz, Germany

Scanning Tunneling Microscope (STM) and Spectroscopy (STS) are used to study the adsorption geometry and electronic structure of isolated hexafluoro-cobalt phthalocyanine (F16CoPc) molecules adsorbed on the basal plan of HOPG and Ag(110). Monolayers were prepared using organic molecular beam epitaxy (OMBE) under ultra high vacuum (UHV) conditions at room temperature and investigated at 45 K using Omicron VT-STM. F16CoPc forms a perfect quadratic superstructure independent of the substrate. In both cases a planar adsorption of molecules is observed with a non-commensurate superstructure with the substrate lattice. Moreover tunneling voltage polarity dependent contrast reversal at the cobalt center is observed, especially in the case of molecules on Ag(110). Adsorption geometry of molecules within the adlayer shows the influence of fluorine atoms in the packing. Tunneling spectroscopy and single molecule calculations are employed to understand the type of interactions between F16CoPc and the substrate, as well as the effects of fluorine atoms on the geometric configurations of the adsorbed F16CoPc molecules.

O 51.9 Wed 17:15 MA 041

Ordered 2D assemblies of phenoxy substituted phthalocyanines as hosts for further guest molecules — TOMAS SAMUELY¹, SHI-XIA LIU², NIKOLAI WINTJES¹, MARCO HAAS², SILVIO DECURTINS², THOMAS A. JUNG^{1,3}, and ●MEIKE STÖHR¹ — ¹Institute of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland — ²Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012-Bern, Switzerland — ³Laboratory for Micro- and Nanostructures, Paul-Scherrer-Institute, 5232 Villigen, Switzerland

Symmetrically substituted phthalocyanines (Pcs) with eight peripheral di-(tert-butyl)phenoxy (DTPO) groups self-organize on Ag(111) and Au(111) substrates into various phases. These phases coexist due to a retardation of the thermodynamic optimization of the conformations, caused by the proximity of the Pc core to the metal substrate together with the steric entanglement between neighboring DTPO substituents. The rotational degrees of freedom allow all the DTPO substituents

to be arranged above the plane of the Pc core, forming a bowl-like structure, which enables the interaction of the Pc core with the metal substrate. Moreover, this bowl-like shape predetermines such assemblies to serve as a host accommodating guest molecules. As an example, C60 molecules, upon deposition on an ordered layer of the DTPO substituted Pcs, bind to two clearly distinguishable sites, exhibiting different morphological and electronic properties. Since Pcs are well-known electron donors and C60 molecules are good electron acceptors, such ordered guest-host systems allow addressable STM/STS investigations of individual donor-acceptor complexes.

O 51.10 Wed 17:30 MA 041

Adsorption and ordering of a triphenylene Cr(CO)₃ complex on noble metal surfaces — ●CHRISTOPH H. SCHMITZ¹, JULIAN IKONOMOV¹, IORDAN KOSSEV¹, CAROLA RANG², SERGUEI SOUBATCH³, OLGA NEUCHEVA³, FRANK STEFAN TAUTZ³, KARL HEINZ DÖTZ², and MORITZ SOKOLOWSKI¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Bonn — ²Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn — ³Institute of Bio- and Nanosystems 3, Forschungszentrum Jülich

Adsorption by physical vapor deposition of metal-organic complexes is so far known for metallocene- and phthalocyanine-derivatives. Here we report on the deposition of the chromium complex (1,2,3,4,4a,12b)-tricarboxyl-(2,3-diethyl-1,4-dimethoxytriphenylene)chromium(0) (TPHC) and the corresponding ligand 2,3-diethyl-1,4-dimethoxytriphenylene (TPH). This complex is of interest, since a haptotropic migration of the Cr(CO)₃-moiety is found in solution and may also be present in adsorbed layers. We succeeded to prepare ordered layers of TPHC and TPH on silver and copper single crystal surfaces that were investigated by scanning tunneling microscopy and x-ray photoelectron spectroscopy. STM shows the formation of long range ordered structures with different unit cells for TPHC and TPH. This demonstrates that the Cr(CO)₃-moiety has a decisive influence on the lateral interaction of the molecules on the surface. XPS results reveal the intact adsorption of TPHC. Experiments with low energy electron diffraction, however, fail since a decomposition of the complex due to electron bombardment occurs. (Funded by DFG SFB 624)

O 51.11 Wed 17:45 MA 041

Local and Long Range Structure of Ferrocene on Au(111) Surfaces — ●GERHARD PIRUG¹, MICHEL KAZEMPOOR¹, JOSEF MYSLIVEČEK², and BERT VOIGTLÄNDER¹ — ¹Institut für Bio- und Nanosysteme (IBN3), Forschungszentrum Jülich GmbH, Germany — ²Dept. of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University Prague, Czech Republic

The adsorption of ferrocene (Fe(C₅H₅)₂) on Au(111) surfaces has been studied spectroscopically applying HREELS and structurally by means of LEED and STM. The vibrational modes observed by HREELS indicate reversible molecular adsorption at temperatures of about 110 K. The corresponding frequencies are not significantly shifted with respect to IR or Raman data for solid ferrocene, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be distinguished from the physisorbed first layer based on relative intensity changes of vibrational modes. In the monolayer regime vibrational modes with a perpendicular dipole moment from more or less upright standing ferrocene molecules dominate. Dissociation into cyclopentadienyl radicals (C₅H₅) can be excluded. Molecular self assembly yields well ordered surface structures. A commensurate ($3 \times \sqrt{3}$)rect (p2mg) structure has been identified from topographical STM images and LEED pattern, consistently. In addition a compressed incommensurate structure develops. Both structures are at variance with recent findings by Braun et al.¹ but can be related to the crystallographic structure of crystalline ferrocene. (¹K.F. Braun V. Iancu, N. Pertaya, K.H. Rieder and S.-W. Hla, Phys. Rev. Lett. 96, 246102 (2006))

O 51.12 Wed 18:00 MA 041

Interaction of scanning tunneling microscopy tip with adatoms and molecules on metal surfaces: ab initio studies — ●KUN TAO¹, VALERI S. STEPANYUK¹, DMITRI I. BAZHANOV², and PATRICK BRUNO¹ — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — ²Faculty of Physics, Moscow state University, 119899 Moscow, Russia

We perform ab initio calculations of the interaction of the STM tip with magnetic adatoms and molecules on metal surfaces. We apply density functional theory (DFT) based methods (SIESTA, VASP) and perform calculations in the fully relaxed geometries for the tip and the substrate. Both interactions with nonmagnetic and magnetic tips are

studied. We concentrate on 3d transition metal adatoms supported on Cu(100) and Cu(111) surfaces. The interaction of the tip with molecule-metal sandwich, consisting of the benzene molecule and 3d adatom, is discussed. Our study reveals that electronic states and magnetic moments of adatoms can be drastically changed by interaction with tip. We also show that magnetic coupling between the tip and the adatom can be manipulated by approaching the tip to the substrate.

O 51.13 Wed 18:15 MA 041

Surface-selection rule for infrared spectra of adsorbate molecules violated by metal ad-atoms — •OLAF SKIBBE¹, MARTIN BINDER¹, ANDREAS OTTO², and ANNEMARIE PUCCI¹ — ¹Kirchhoff-Institut für Physik, Universität Heidelberg, Im Neuenheimer Feld 227, D-69120 Heidelberg — ²Institut für Physik der kondensierten Materie, Heinrich-Heine Universität, Düsseldorf

Copper adatoms on Cu(111) significantly modify the infrared

reflection-absorption spectrum of ethylene (C₂H₄) on Cu(111). The infrared spectral changes do not involve significant shifts of vibration frequencies as they would be expected for strong distortions. But originally non-infrared active Raman modes of the centrosymmetric molecule appear in the spectra and the infrared active CH₂-wagging mode disappears already below 0.2 monolayers of Cu adatoms. High-resolution electron energy loss spectra of adsorbed ethylene for various Cu-adatom pre-coverage show the same vibration lines and indicate the change in their dipole character. Since the molecules are obviously unchanged, the Raman lines in the infrared spectra must get their dynamic dipole moment from transient electron transfer favored by atomic disorder on the metal surface, which is an experimental proof of a previous hypothesis. The completely new and surprising result of this work is the disappearing infrared active mode at sub-monolayer Cu-adatom coverage, which we explain by screening due to the background polarizability increased by Cu adatoms.