Molecular 2D Ordering of Viologens Under Non-Equilibrium Condition - an EC-STM Approach — DUC THANH PHAM, KLAUS KANDEL, and FERDINAND BRINKMANN — Institut f. Physikalishe und Theoretische Chemie, Uni Bonn

The structural characterization of 1,3-di(benzyl-4,4'-bipyriddylium molecules (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 DBV, while in the double layer regime resulting in the surface assisted organization of a cationic DBV + 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 monocation viologen takes place, a "reactive" adsorption of viologens occurs. Preferred reaction products at the surface are metastable viologen dimer species with a viologen coverage of 0.077 ML obtained under kinetic control. This dimer phase exhibits an unusually high stability against changes of the potential. It can only be converted reversibly into either the oxidized dicationic species or the more compact and thermodynamically favorable "polymeric" stacking phase of radical monocation-s by significantly more anodic or cathodic potentials sweeps, respectively.

Ultra-thin films of α-conjugated molecule on Au(001) at room and elevated temperature — ANKE HÖPER, KLAUS DUNCKER, MARIO KIEL, SEBASTIAN WEDEKIND, RENÉ HAMMER, and WOLF WIDORA — Institut f. Physik, Martin-Luther-Universität Halle-Wittenberg

The rodlike π-conjugated molecule α-sexithiophene on Au(001) 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 surfaces areas with quenched and conserved reconstruction. [1] M. Kiel, K. Duncker, Ch. Hagendorf, W. Widora, Phys. Rev. B 75, 195439 (2007)

Formation of covalently bound chains from Dibromotetfluorene molecules on Au(111) — LIEF LÄFFERZEN1, HAO YU2, STEFAN HECHT3, and LEONHARD GRILL3 — 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 prespecified 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 Dibromotetfluorene (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. Laufferentz, M. Persson, M. V. Peters, and S. Hecht, Nature Nanotech. 2, 687 (2007)

Protection group controlled surface chemistry-organization and heat induced coupling of diphenyl derivatives on metal surfaces — SERPIL BOZ1, MEIKE STÖHR1, UMIT SOYDANER2, and MARCEL MAYOR2 — 1University of Basel, Department of Physics, Klingelbergstrasse, CH-4056 Basel, Switzerland; 2University of Basel, Department of Chemistry, St. Johanner 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 macro-molecules. 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.

Thermally induced polymerization of molecules on surfaces — MANFRED MATENA1, JORGE LOHO-CHICA1, MEIKE STÖHR1, KATHRIN MÜLLER2, THOMAS A. JUNG2, TILL RIEH2, and LUTZ H. GADE2 — 1Department Physik, Universität Basel, Switzerland; 2Paul-Scherrer-Institut, Villigen, Switzerland

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 polyaramatic chains.
STM and STS on Ultrathin Organic Layers of Fluorinated ion. We will discuss our results on the growth morphology in terms of scope. Molecules have been deposited at room temperature to allow has been studied by a variable-temperature scanning tunneling microscope. shows site specificity, i.e. the Fe atom adsorbs on top of a Cl− as assembling was observed, while at high coverages (>) 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 aliphatic C60 molecules. The interaction between the substrate and 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).

STM and STS on Ultrathin Organic Layers of Fluorinated Cobalt Phthalocyanine (F16CoPc) on Crystals Surfaces — MAHMOUD ABDEL-HAFEZ, MARIUS TOADER, THIRUVANCHERIL GOPAKUMAR, and MICHAEL HiETSCHOID — 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 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 fluorene 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 fluorene atoms on the geometric configurations of the adsorbed F16CoPc molecules.

Ordered 2D assemblies of phenox substituted phthalocya- nines as hosts for further guest molecules — TOMAS SAMUEL1, SHI-XIA Li2, NIKOLAI WINTJES1, MARCO HAAS1, SILVIO DECREUTS2, THOMAS A. JUNGL1, and MEIKE STÖHR1 — 1Institute of Physics, University of Basel, Klingelbergstrasse 42, Basel, Switzerland 2Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012-Bern, Switzerland — Laboratory for Micro- and Nanostructures, Paul-Scherrer-Institute, 5232 Villigen, Switzerland Symmetrically substituted phthalocyanines (Pcs) with eight peripheral di-([tert-butyl]phenox (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 sub- stituted Pcs, bind to two clearly distinguishable sites, exhibiting differ- ent morphologic 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.

Adsorption and ordering of a triphenylen chromium (Cr(CO)3) comp lex on noble metal surfaces — CHRISTOPH H. SCHMITZ1, JULIAN IOKONOVSKY2, IORDAN KOSKESN3, CAROLLA RANCZ4, SERGUIY SOURABCH5, OlgA NECHvation6, FRANK STEFAN TAUTZ7, KARL HEINZ DÖTZ7, 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 metalloocene- and phthalocyanine-derivatives. Here we report on the deposition of the chromium complex (1,2,3,4,4a,12b)- tetraphenyl-2,3,5,6-diepoxytriphenylmethane/chromium(0) (TPHC) and the corresponding ligand 2,3-diepoxy-1,4-dimethoxy-triphenyl-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 using 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)

Local and Long Range Structure of Ferrocene on Au(111) Surfaces — GERHARD PIRIG1, MICHIEL KAZEMPOON2, JOSEF MYS-LIVCEVA3, and BERT VOGTLANDER1 — 1Institut für Bio- und Nanosyste mes (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 affected with respect to IR or Raman data for solid ferrocene, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be dis- tinguished from the physiosorbed 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)H2 can be excluded. Molecular self assembly yields well ordered surface structures. A commensurate (3 x 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 in accordance with previous findings by Braun et al. but can be related to the crystallographic structure of crystalline ferrocene. (K.F. Braun, V. Iancu, N. Pertaya, K.H. Rieder and S.-W. Hla, Phys. Rev. Lett. 96, 246102 (2006))

Interaction of scanning tunneling microscopy tip with adatoms and molecules on metal surfaces: ab initio studies — KUN TAG1, VALERI S. STEPANUK1, DMITR I. BAZHANOVO2, 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.

Surface-selection rule for infrared spectra of adsorbed molecules violated by metal ad-atoms — Olaf Skibbe1, Martin Binder1, Andreas Otto2, and Annemarie Pucci1 —

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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.