

O 88: Metal substrates: Adsorption of organic / bio molecules IX

Time: Thursday 17:15–19:30

Location: PHY C213

O 88.1 Thu 17:15 PHY C213

2D Nanoporous networks based on simultaneous expression of H-Bonds and Metal-Coordination — ●SUSHOBHAN JOSHI¹, SARANYAN VIJAYARAGHAVAN¹, DAVID ECIJA¹, WILLI AUWÄRTER¹, KNUD SEUFERT¹, CLAUDIA AURISICCHIO², DAVIDE BONIFAZI², and JOHANNES V. BARTH¹ — ¹Physik Department, E20 Technische Universität München, D-85748 Garching, Germany — ²Department of chemistry, University of Namur, Namur B-500, Belgium

The control and understanding of self assembly protocols is a prerequisite to realize tailored stable molecular networks with novel functional properties. In particular, well defined metal surfaces have been employed as platforms to build highly regular 2D coordination networks, including porous patterns suitable for hosting guest species. Here we present an STM study of supramolecular architectures based on a de novo synthesized three fold symmetric molecule with 3 identical functional terminal pyridyl groups. They are instrumental for the development of porous networks stabilized by N...H hydrogen bonds and pyridyl Cu coordinations on Ag(111) and Cu(111) in UHV conditions. On Ag(111) a close packed layer is seen and subsequent Cu deposition essays three different coordination structures. Two of the structures are based on both N...H Hydrogen bonds and Cu coordination and one is exclusively stabilized by Cu coordination. A glassy porous network was seen on Cu(111) substrate where the network topology is based again on both H-bonding and the linear pyridyl-Cu-pyridyl motifs.

O 88.2 Thu 17:30 PHY C213

Multi-component alternating nanostructures of functional organic molecules with adjustable feature size — ●DINGYONG ZHONG, LIFENG CHI, and HARALD FUCHS — Physikalisches Institut and Center for Nanotechnology (CeNTech), Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany

Since the diffusion length of excitons in organic semiconducting materials is typically in the range of ten(s) nanometers, segregation of different functional organic molecules in such length scales is of importance to promote electron-hole separation and therefore increasing the energy conversion efficiency of organic photovoltaic devices. Here we report a bottom-up strategy for fabricating multi-component alternating organic nanostructures based on the pre-template effect of vicinal surfaces. Two and three dimensional multi-component alternating nanostructures up to four components have been fabricated and analyzed by scanning tunneling microscopy. The feature size of the nanostructures is tunable from about ten to several tens nanometers by adjusting the processing temperatures.

O 88.3 Thu 17:45 PHY C213

Self-Assembly of Melem on Ag(111) - emergence of porous structures based on amino-heptazine hydrogen bonds — ●JOHANNA EICHHORN¹, STEFAN SCHLÖGL¹, BETTINA V. LOTSCH¹, WOLFGANG M. HECKL², and MARKUS LACKINGER¹ — ¹Ludwig-Maximilians-University and Center for Nanoscience (CeNS), Munich, Germany — ²Deutsches Museum, Munich, Germany

Supramolecular self-assembly has been proven to be a powerful bottom-up technique for surface functionalization. In particular, two-dimensional nanoporous networks have attracted broad interest. Depending on the molecular building blocks, size and shape of cavities can be tuned. Many porous structures are stabilized by intermolecular hydrogen bonds between carboxylic acids. Yet, on more reactive substrates, carboxylic acids often bind strongly to the surface which hampers network formation. Therefore, we investigate less reactive building blocks for nanoporous networks on more reactive surfaces. In this respect amino groups in combination with heterocycles offer a promising alternative.

We studied self-assembly of melem, a triply amine functionalized heptazine ring, on Ag(111) by means of UHV-STM. Three different polymorphs were observed, where two structures exhibit pores with a diameter of ~1.5 nm. Each of those pores is bordered by six melem molecules interconnected by hydrogen bonds between amino groups and nitrogen in the heptazine ring. One of the porous structures exhibits two molecules per unit cell with a dimer as basic structural motif, while the densely packed polymorph exhibits only one molecule per unit cell.

O 88.4 Thu 18:00 PHY C213

Hierarchical interactions - network formation of organic molecules on graphene/Ru(0001) — ●MICHAEL ROOS¹, DANIELA KÜNZEL², HARRY E. HOSTER^{1,3}, AXEL GROSS², and R. JÜRGEN BEHM¹ — ¹Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany — ²Ulm University, Institute of Theoretical Chemistry, 89069 Ulm, Germany — ³Current address: Technische Universität München, Centre for Electromobility, 50 Nanyang Drive, Singapore 637553

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded 2D networks on solid surfaces. The hydrogen bond configurations and therefore the resulting structures are steered via the positions of the nitrogen atoms within the BTP molecules. On smooth surfaces such as graphite or metal single crystals, the molecule-substrate interactions play a secondary role for the structure formation, mainly by determining the rotational orientations of the ordered networks. In this contribution, we demonstrate that more pronounced template effects arise for substrates where the molecule-substrate interaction varies laterally at the nanometer scale. As an example, we will show the ordering behavior of BTP molecules on graphene monolayers grown on Ru(0001). Submolecularly resolved STM images show that the BTP molecules are confined to the valleys of the graphene. We will compare the resulting supramolecular assemblies with the ordered 2D networks formed by the same molecules on smooth substrates, and will discuss the effect of the template quantitatively by means of force field calculations and supporting thermal desorption experiments.

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Temperature Induced Phase Transition of Pentacene Sub-Monolayers on Cu(110)-(2x1)O — ●JOHANNES GALL, MICHAEL HOHAGE, LIDONG SUN, DANIEL QUETESCHNER, GÜNTHER WEIDLINGER, MARIELLA DENK, and PETER ZEPPENFELD — Institute of Experimental Physics, Johannes Kepler University, Linz, Austria.

A reversible temperature induced phase transition of pentacene sub-monolayer films on the Cu(110)-(2x1)O reconstructed substrate was observed by means of Reflectance Difference Spectroscopy (RDS). It is interpreted as a transition from a 2D condensed phase (stable at low temperatures) to a molecular 2D gas phase at high temperatures.

In the present study, we have performed Monte Carlo (MC) and Kinetic Monte Carlo (KMC) simulations in the framework of a rectangular two dimensional lattice-gas model with nearest neighbor interactions to reproduce the phase transition behavior.

From adsorption isotherm experiments of pentacene on Cu(110)-(2x1)O, the 2D-sublimation energy of pentacene was found to be 87 meV. In contrast, from simulations, the sum of the lateral molecule-molecule interaction energies of pentacene was determined to be 101 meV.

However, from the RD spectra and Scanning Tunneling Microscopy (STM) images evidence was found that the gas phase actually consists of pentacene dimers. Therefore, the influence of these dimers on the phase transition is discussed.

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Growth and thermal evolution of ultrathin NTCDA films on Ag(111) studied by FT-IRAS and TPD — ●CAROLIN R. BRAATZ, GREGOR ÖHL, and PETER JAKOB — Philipps-Universität Marburg

The growth and thermal evolution of ultrathin films of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) adsorbed on Ag(111) was investigated by Fourier-transform infrared absorption spectroscopy (FT-IRAS) and thermal desorption. The films were grown by organic molecular beam deposition in an UHV environment and analyzed in situ. Results will be presented for coverages from the sub-monolayer to the lower multilayer regime and in a wide temperature range (20 - 500 K). Depending on growth conditions and annealing temperatures a variety of different phases could be identified from their characteristic vibrational signatures, allowing us to track related phase transformations in detail. Thereby, a parallel oriented metastable phase is observed prior to (crystalline) multilayer formation.

O 88.7 Thu 18:45 PHY C213

Face-dependent chemisorption bondlengths for the formate

species on copper. — •DAGMAR KREKEMEYER-LORENZO¹, MATT BRADLEY², WERNER UNTERBERGER¹, DAVID DUNCAN², TSENOLO LEROTHOLI², JIM ROBINSON², and PHIL WOODRUFF² — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of Warwick, England

Chemisorption bondlengths of molecules at metal surfaces have been shown in the past to be dependent on the bond order or coordination number according to a Pauling-like relationship, independent of the crystal face. However, we report here the results of measurements that show a rather strong face-dependence. Specifically, we have investigated the adsorption of the formate species (HCOO), a surface intermediate of the catalytic decomposition of formic acid (HCOOH) on Cu (110) and Cu (111) using the well-established technique of scanned-energy mode photoelectron diffraction (PhD). By using the same technique to study the same adsorbate on the two different faces, we eliminate possible sources of systematic error. Formate is found to adopt the same local bridging geometry (with the O atoms in off-atom sites) on both surfaces, but the associated Cu-O bondlengths are found to be 1.99 Å on Cu(111) and 1.90 Å on Cu (110). The difference must be attributed to more open structure of the Cu(110) surface, on which the surface Cu atoms have lower coordination to the underlying bulk and are surrounded by a lower valence charge density due to Smoluchowski smoothing. Preliminary DFT calculations reproduce the effect qualitatively, but predict a significantly smaller bondlength difference.

O 88.8 Thu 19:00 PHY C213

K-resolved Inverse Photoemission on ultrathin PTCDA/Ag(110) films — •DIRK HAUSCHILD¹, MARKUS SCHOLZ¹, PETER PUSCHNIG², ACHIM SCHÖLL¹, and FRIEDRICH REINERT^{1,3} — ¹Universität Würzburg, Experimentelle Physik VII, D-97074 Würzburg, Germany — ²University of Leoben, Chair of Atomistic Modelling and Design of Materials, A-8700 Leoben, Austria — ³Karlsruhe Institut für Technologie (KIT), Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe, Germany

The occupied valence regime of metal-organic interfaces has been intensively studied by e.g. angular resolved UV-photoelectron spectroscopy allowing direct identification of molecule-metal hybrid states due to interfacial interaction [1]. However, the unoccupied valence levels are

much more complicated to access experimentally limiting the knowledge about the contribution of these orbitals on the interface bonding. K-resolved Inverse Photoelectron Spectroscopy (KRIPES) is a technique to study the unoccupied density of states of inorganic materials. We present the first KRIPES-measurement on an organic monolayer adsorbed on a metal surface and discuss the applicability of KRIPES on orbital tomography established for PES. The single-domain monolayer system PTCDA/Ag(110) shows two non-dispersing states. Comparison of the experimental variation of the KRIPES-spectra intensity and DFT calculation of the free PTCDA molecule identifies the first state as the LUMO+1. The origin of the second state is not clear yet but shows influences of LUMO+1 and LUMO+2.

[1] J. Ziroff *et. al.*, Phys. Rev. Lett., **104**, 233004 (2010)

O 88.9 Thu 19:15 PHY C213

Impact of spontaneous structural imperfection on the energy level alignment — •TAKUYA HOSOKAI¹, HIROYUKI MACHIDA², ALEXANDER GERLACH¹, SATOSHI KERA², NOBUO UENO², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Germany — ²Graduate School of Advanced Integration Science, Chiba university, Japan

We report that structural imperfection in an organic layer affects the electronic structure to result in a serious band-bending in the organic layer and change in the energy level alignment (ELA). Ultraviolet photoelectron spectroscopy (UPS) and metastable atom electron spectroscopy (MAES) were adopted to investigate the thickness dependence of the valence electronic structure and molecular orientation of polar phthalocyanine molecules (chlorogallium phthalocyanine) in thin films grown on graphite. We observed a large band-bending-like shift of occupied molecular orbital bands towards the Fermi level and the vacuum level increases continuously for the as-grown film, whereas these phenomena were considerably less pronounced after annealing the film. High-resolution UPS and MAES measurements showed that structural defects, i.e. Cl-up molecules in bilayer domain boundaries, are the origin of the change in the ELA. Our results indicate that controlling the spontaneous structural imperfection is a key for the desired energy level alignment of polar organic thin films on this substrate.