

## O 9 Organic films I

Time: Monday 15:00–17:45

Room: TRE Phys

O 9.1 Mon 15:00 TRE Phys

**STM and LEED studies of  $\alpha$ -sexithiophene on Au(111)** — ●MARIO KIEL, KLAUS DUNCKER, CHRISTIAN HAGENDORF, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, FB Physik, D-06120 Halle(Saale)

The growth of  $\alpha$ -sexithiophene (6T) on the close-packed Au(111) surface has been studied by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The evaporation of the 6T molecules from a home-built Knudsen cell and measurements have been performed at a base pressure of  $1 \times 10^{-10}$  mbar. STM images reveal rows of equivalent 6T molecules with one molecule per unit cell. The rows are rotated by  $9^\circ$  with respect to the  $[11\bar{2}]$  direction and span large Au(111) terraces ( $\sim 100$  nm). Six symmetry-equivalent domains are possible, however step-induced structures with the molecular axis along the step edges are strongly favored. This can be also seen by higher spot intensities in LEED, visible due to a small crystal miscut. On the terrace, the herringbone ( $22 \times \sqrt{3}$ ) reconstruction of the clean Au(111) surface is stretched by about 15% upon 6T monolayer adsorption. This is interpreted as adsorbate-induced strain in the first Au(111) layer.

O 9.2 Mon 15:15 TRE Phys

**Comparison of gas- and condensed phase NEXAFS spectra of large organic molecules** — ●FLORIAN HOLCH<sup>1</sup>, DOMINIQUE HÜBNER<sup>1</sup>, ACHIM SCHÖLL<sup>1</sup>, RAINER FINK<sup>2</sup>, and EBERHARD UMBACH<sup>1</sup> — <sup>1</sup>Universität Würzburg, Experimentelle Physik II — <sup>2</sup>Universität Erlangen, Physikalische Chemie II

The interaction between most large organic molecules in the solid state is commonly believed to be solely due to electrostatic and van-der-Waals forces. An analysis of these intermolecular effects requires a comparison of high-quality spectroscopic data of gaseous and condensed organic molecules. In this work we present high-resolution NEXAFS spectra of 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride (NTCDA) and acenaphthenequinone (ANQ) in the gas phase and solid state. For the gas phase experiments a new experimental set-up has been used that allows the measurement of substances with high sublimation temperatures. A detailed Franck-Condon analysis of the *vibronic* fine structure of the NTCDA spectra at the C K-edge yields consistent results for both phases. In contrast, pronounced differences in the *electronic* features between gas phase and condensate can be demonstrated. This corroborates the results for ANQ that also suggest an involvement of the  $\pi^*$ -orbitals of the aromatic core in the intermolecular interaction. Our findings thus indicate that intermolecular forces can be much stronger than commonly believed and may even cause the formation of intermolecular bonds. The project is financed by the BMBF under contract 05KS4WWC/2

O 9.3 Mon 15:30 TRE Phys

**Long-range order and polymerisation of sexithiophene on Ag(100) surfaces – a STM study** — ●KLAUS DUNCKER, SEBASTIAN WEDEKIND, CHRISTIAN HAGENDORF, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Fb Physik

High-temperature scanning tunneling microscopy (STM) is used to study the morphology of the first few monolayers of  $\alpha$ -sexithiophene (6T) on Ag(100) surfaces at room and elevated temperatures. The 6T molecules have been evaporated from a homebuilt Knudsen cell at a base pressure of the UHV chamber of  $1 \times 10^{-10}$  mbar.

Several molecular superstructures coexist in different domains within the monolayer. They can be divided into two groups with either one or two molecules in the unit cell. Common to all, the flat-lying 6T molecules are oriented with their long axis parallel to  $[011]$  and  $[01\bar{1}]$  crystallographic directions of the Ag-substrate. As the predominant superstructure with two molecules in the unit cell we find a  $(9/0)(2/5)$  structure with a pair of chirally equivalent, parallel molecules in the unit cell. Additionally, a herringbone-like structure is found with two non-linear molecules in the unit cell forming rows in highly-ordered domains. STM images with submolecular resolution reveal flat molecules which have undergone a cis-trans isomerization exclusively between the 4th and 5th thiophene ring and which align in rows of left- and right-handed molecules.

Whereas earlier studies indicate molecular dissociation of the first monolayer during thermal desorption, we have identified by STM polymerization to long chains and polythiophene networks after annealing to about 440 K and multilayer desorption.

O 9.4 Mon 15:45 TRE Phys

**Novel Tripod Ligands for Prickly Self-Assembled Monolayers** — ●TOBIAS WEIDNER<sup>1</sup>, ANDREAS KRÄMER<sup>2</sup>, MICHAEL ZHARNIKOV<sup>3</sup>, ANDREY SHAPORENKO<sup>3</sup>, DOMINIK ENDERS<sup>4</sup>, ULRICH SIEMELING<sup>2</sup>, and FRANK TRÄGER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Kassel, Kassel — <sup>2</sup>Institut für Chemie, Universität Kassel, Kassel — <sup>3</sup>Angewandte Physikalische Chemie, Universität Heidelberg, Heidelberg — <sup>4</sup>Kirchhoff Institut für Physik, Universität Heidelberg, Heidelberg

Self-assembled monolayers (SAMs) consisting of laterally separated and non-interacting functional units are of great current interest in sensor- and molecular electronics applications. We used the new ligands PhSi(CH<sub>2</sub>SMe)<sub>3</sub> (**1**) and Ph-*p*-C<sub>6</sub>H<sub>4</sub>-Si(CH<sub>2</sub>SMe)<sub>3</sub> (**2**) to prepare such SAMs on gold. In **1** and **2** the rigid rod type units Ph and Ph-*p*-C<sub>6</sub>H<sub>4</sub>, respectively, are connected to the central Si atom at the vertex of the tripodal binding unit that can be anchored on the surface with three instead of a single binding site via thioether head groups. In particular, owing to the relative size of the binding unit, the SAMs are expected to exhibit considerable void space between individual Ph and Ph-*p*-C<sub>6</sub>H<sub>4</sub> units which protrude from the surface.

Film formation was investigated *in situ* by optical second harmonic generation and ellipsometry, revealing a two-step process. SAMs of **2** were further investigated by *ex situ* methods, *viz.* high-resolution XPS (HRXPS), IR-spectroscopy, and STM. The most important results are as follows: HRXPS showed three different binding states of sulfur. Dense packing of the tripodal anchor groups on the surface has been verified with a substantially lower density of the biphenyl pricks.

O 9.5 Mon 16:00 TRE Phys

**Molecule-molecule vs. molecule-substrate interactions in 2D oligopyridine networks** — ●H.E. HOSTER<sup>1</sup>, M. ROOS<sup>1</sup>, CH. MEIER<sup>2</sup>, A. BREITRUCK<sup>1</sup>, B. PLUHAR<sup>1</sup>, M. SEYFRIED<sup>1</sup>, K. TONIGOLD<sup>1</sup>, and R.J. BEHM<sup>1</sup> — <sup>1</sup>Abt. Oberflächenchemie und Katalyse, Universität Ulm, 89069 Ulm — <sup>2</sup>Abt. Organische Chemie III, Universität Ulm, 89069 Ulm

Oligopyridines vapor deposited onto single crystalline surfaces form highly ordered 2D networks with a geometry mainly determined by the coverage. We have analysed such networks on HOPG, Au(111), and Ag(111)-like adlayers on Ru(0001). Variations of the substrate in some cases alter details within the structures such as intermolecular distances or aspect ratios of unit cells, while in other instances certain molecular arrangements are only found on one type of surface. We assume the local constellations of the molecules and as a consequence also the unit cells of the resulting superstructures to be dominated by intermolecular interactions via hydrogen bonds. On the other hand, both the 2D networks and the planar single molecules appear to prefer certain lateral alignments with respect to the substrate, as obvious in closer analyses of domain orientations and STM-images showing molecular adlayers with the Au(111) herringbone reconstruction shining through. This points towards a significant contribution of the adlayer/substrate interface to the overall energy, which causes an adaptation of the respective 2D-layer to the respective substrate up to a repetitive occupation of equivalent adsorption sites, *i.e.*, a commensurate or at least quasi-epitaxial layer.

O 9.6 Mon 16:15 TRE Phys

**Two step adsorption of phenyl-functionalized tripod ligands on gold** — ●TOBIAS WEIDNER<sup>1</sup>, ANDREAS KRÄMER<sup>2</sup>, TIGRAN VARTANYAN<sup>3</sup>, ULRICH SIEMELING<sup>2</sup>, and FRANK TRÄGER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Kassel, Kassel — <sup>2</sup>Institut für Chemie, Universität Kassel, Kassel — <sup>3</sup>Vavilov State Optical Institute, St Petersburg, Russia

Further progress in organic monolayer preparation depends on the thorough understanding of thin film formation processes. In this contribution *in situ* optical second harmonic generation (SHG) measurements have been employed to study the adsorption kinetics of the new tripodal thioether ligands PhSi(CH<sub>2</sub>SMe)<sub>3</sub> and Ph-*p*-C<sub>6</sub>H<sub>4</sub>-Si(CH<sub>2</sub>SMe)<sub>3</sub> on gold substrate from solution. Previous characterization by *in situ* ellipsometry and a number of *ex situ* methods, *viz.* high-resolution XPS, FTIR-RAS, and STM indicated dense packing of the tripodal anchor groups on the surface with a substantially lower density of the biphenyl moieties. To characterize the adsorbate-substrate interaction quantitatively a new method based on SHG measurements at different temperatures was developed. The rate of adsorption was found to decrease from  $2.4 \cdot 10^{-3} \text{ s}^{-1}$

to  $3.4 \cdot 10^{-4} \text{ s}^{-1}$  when the solution temperature was raised from 2.5 to 49 degrees centigrade (at constant concentration). This contra intuitive behavior is explained by a two-step adsorption model assuming that stable chemical bonds are formed subsequent to a weakly bound precursor state. The theoretical description of such a model allows us to obtain an estimate of the enthalpy of the physisorbed state, a parameter difficult or impossible to determine by other techniques.

O 9.7 Mon 16:30 TRE Phys

**Coverage dependent structure of 2D networks formed by oligopyridines on Ag(111)/Ru(0001) Bonds** — ●ACHIM BREITRUCK<sup>1</sup>, MATTHIAS ROOS<sup>1</sup>, CHRISTOPH MEIER<sup>2</sup>, ULRICH ZIENER<sup>2</sup>, MONA SEYFRIED<sup>1</sup>, HARRY E. HOSTER<sup>1</sup>, and ROLF J. BEHM<sup>1</sup> — <sup>1</sup>Department Surface Chemistry and Catalysis, University of Ulm, 89069 Ulm — <sup>2</sup>Department Macromolecular Chemistry and Organic Materials, University of Ulm, 89081 Ulm

Oligopyridines form highly ordered 2D networks on a number of single crystal surfaces [1]. They are of interest both for the physical background of their structure formation itself and for their possible utilization as self assembling templates for nanostructuring. In the present study, layers of increasing coverage have been vapor deposited in UHV onto Ag(111)-like adlayers on Ru(0001). STM analyses reveal at least 5 different highly ordered structures, with a geometry depending on the coverage and, in some cases, the temperature during and after deposition. The coverage dependence is an immediate consequence of the geometry of the utilized oligopyridines, which at higher packing densities forces the molecules into local constellations with less network stabilizing hydrogen bonds per molecule. This also involves a coverage dependent adsorption energy, which allows to saveily transform one structure into another by partial desorption of the adlayer.

[1] U. Ziener, J.-M. Lehn, A. Morran, M. Möller, Chem. Eur. J., 2002, 8(4), 951-957

O 9.8 Mon 16:45 TRE Phys

**High thermal stability of electron cross-linked aromatic self-assembled monolayers** — ●MOHAMED EL-DESAWY, ANDREY TURCHANIN, and ARMIN GÖLZHÄUSER — Physik Supramolekularer Systeme, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld

We report on the thermal stability of e-beam cross-linked biphenylthiol (BPT) self-assembled monolayers (SAMs) on gold surfaces. The monolayers were formed from solution and cross-linked by low-energy electrons (50-200 eV). The SAMs were then thermally annealed in ultra high vacuum. Long annealing times and slow heating rates were employed to follow temperature induced changes at conditions close to thermal equilibrium. After each heating step, the films were analyzed by X-ray photoelectron spectroscopy (XPS). For non cross-linked BPT, at  $\sim 420\text{K}$  the carbon coverage abruptly decreases to  $\sim 20\%$ , which is accompanied by a breaking of C-S bonds. In cross-linked BPT, despite a C-S bond cleavage in the same temperature range, the carbon matrix shows only gradual changes with increasing temperature. Even at  $\sim 1000\text{K}$ , the SAM coverage has only decreased to  $\sim 80\%$ . Hence, cross-linked SAMs show a much higher thermal stability than non cross-linked ones. This is of importance for technological applications of SAM coatings.

O 9.9 Mon 17:00 TRE Phys

**On the Origin of a Phase Transition in clean Porphyrin Films on a Silver (111) Surface** — ●H. MARBACH, K. COMANICI, F. BUCHNER, F. MAIER, and H.-P. STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91056 Erlangen

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. The properties of porphyrins can be modified e.g. by introducing or changing a central metal atom and different ligands. We studied different porphyrins on a silver (111) surface by means of scanning tunneling microscopy (STM) in ultra high vacuum (UHV). The preparation of the porphyrin layers was done in UHV via sublimation techniques. Different ordered phases and spatiotemporal behaviors were observed for different central metal atoms and porphyrin ligands. In particular for a specific Cobalt porphyrin (Co-TTBPP) two different phases (square and hexagonal) were observed. In a time series of STM images the transition from the hexagonal to the square phase was studied. Based on these observa-

tions and the comparison with the ordered square structures of similar porphyrins the underlying mechanism is interpreted as an activated process.

O 9.10 Mon 17:15 TRE Phys

**Electroless metal deposition on the surface of aromatic self-assembled monolayers** — ●CHRISTOPH T. NOTTBOHM, ANDREY TURCHANIN, and ARMIN GÖLZHÄUSER — Physik Supramolekularer Systeme, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld

We investigated the palladium-catalysed electroless deposition (ELD) of copper on amino-terminated, cross-linked biphenyl self-assembled monolayers (SAMs). Cross-linking as well as the generation of surface amino groups is achieved by irradiation with low-energy electrons. The cross-linked SAM acts as a diffusion barrier, suppressing the catalyst-free ELD of copper on the gold substrate. Immobilization of a catalyst on the surface of the SAM is achieved by the reduction of Pd(II) ions that are coordinated to the surface amino groups. This was verified by angle resolved X-ray photoelectron spectroscopy (APXPS). Using a stencil mask to locally generate surface amino groups, it was shown by atomic force microscopy that copper is only deposited in irradiated areas. This indicates that copper deposition occurs only at the catalytic site.

O 9.11 Mon 17:30 TRE Phys

**Temperature effect in branching of photochemical reactions** — ●ZHARNIKOV MICHAEL<sup>1</sup>, ANDREY SHAPORENKO<sup>1</sup>, ANDREA BAUMER<sup>2</sup>, DIETRICH MENZEL<sup>3</sup>, and PETER FEULNER<sup>3</sup> — <sup>1</sup>Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg — <sup>2</sup>Walter Schottky Institut, Am Coulombwall 3, D-85748 Garching — <sup>3</sup>Physikdepartment E20, Technische Universität München, D-85747 Garching

Radiation-induced damage represents a severe constraint for the characterization of organic and biological materials by advanced electron or x-ray spectroscopy and microscopy. A possibility to reduce damage is cooling of the samples down to cryogenic temperatures. The protective effect of cooling is commonly related to hindrance of mass transport in the object, whereas the basic irradiation-induced bond cleavage is believed to be unaffected. To prove this hypothesis we studied radiation damage of self-assembled monolayers, which are prototypes of thin organic layers and highly organized biological systems. We demonstrate that the effect of cooling is twofold. It freezes the structure, but by decreasing the mobility of fragments it also changes the branching of various photochemical reactions, thereby strongly modifying the cross sections as well as the products of irradiation induced processes. Two limiting cases could be identified. Reactions involving transport of single atoms and small fragments proceed nearly independent of temperature. Reactions requiring transport of heavy fragments are, however, efficiently quenched by cooling. We speculate that bonds can recombine if the fragments are forced to stay in place due to their reduced mobility at low temperatures.