

## O 3: Inorganic/Organic Interfaces: Growth I

Time: Monday 10:30–13:00

Location: MA 005

O 3.1 Mon 10:30 MA 005

**Tracking and Removing Br during the Bottom-Up Synthesis of a Graphene Nanoribbon** — ●CHRISTOPHER BRONNER<sup>1,2</sup>, JONAS BJÖRK<sup>3</sup>, and PETRA TEGEDER<sup>1</sup> — <sup>1</sup>Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut — <sup>2</sup>Freie Universität Berlin, Fachbereich Physik — <sup>3</sup>Linköping University, Department of Physics

Thermally induced, two-step bottom-up synthesis from halogen-substituted molecular precursors adsorbed at metal surfaces is an intriguing concept for obtaining graphene nanoribbons with well-defined edge structure and widths on the nanometer scale. The reaction pathways of the dissociated Br atoms have so far not been in the focus of research although they may very well interfere with the on-surface synthesis. Using temperature-programmed desorption we show that Br leaves the surface as HBr in an associative desorption process during the second reaction step, the cyclodehydrogenation. Density functional theory is employed to compare this process to the competing desorption of molecular hydrogen and furthermore shows that prior to desorption, Br is submerged under the three-dimensional intermediate reaction product, polyanthrylene. Upon exposure of this intermediate co-adsorbate to an atmosphere of molecular hydrogen, Br is removed from the surface but the cyclodehydrogenation step is still feasible which demonstrates that Br does not influence the on-surface synthesis. Generally, the ability to remove Br by providing molecular hydrogen opens an effective way to exclude unfavorable influences of the halogen (e.g. side-products, steric effects) in on-surface coupling reactions.

O 3.2 Mon 10:45 MA 005

**Schiff base formation on metal surfaces: towards low dimensional conjugated nanomaterials** — ●LI JIANG<sup>1</sup>, ANTHOULA C. PAPAGEORGIOU<sup>1</sup>, SEUNG CHEOL OH<sup>1</sup>, ÖZGE SAĞLAM<sup>1</sup>, DAVID D. DUNCAN<sup>1</sup>, YI-QI ZHANG<sup>1</sup>, FLORIAN KLAPPENBERGER<sup>1</sup>, SANDEEP MORE<sup>2</sup>, RAJESH BHOSALE<sup>2</sup>, AURELIO MATEO-ALONSO<sup>2,3</sup>, JOACHIM REICHERT<sup>1</sup>, and JOHANNES V. BARTH<sup>1</sup> — <sup>1</sup>TU München, DE — <sup>2</sup>Albert-Ludwigs-Universität Freiburg, DE — <sup>3</sup>Ikerbasqu, ES

Recently, graphene nanoribbons, especially doped with heteroatoms have spurred extensive attention and exploration [1] and covalent organic frameworks (COF) have been successfully synthesized based on Schiff base formation [2]. Inspired by these findings, we systematically investigated the condensation reaction of a tetraamine molecule with a tetraketone molecule on the three coinage close packed metal surfaces Au, Ag and Cu under ultrahigh vacuum conditions by scanning tunneling microscopy. On all three substrates the reactants readily intermix at room temperature forming two-dimensional bi-component networks. We demonstrated the feasibility to form Schiff base conjugated oligomers on the Ag(111) surface by thermal treatment and further investigated the X-ray photoelectron spectroscopy signatures of the reactants and products as a function of the annealing temperature. In contrast to the behavior on Ag(111), the monomers desorb from the Au(111) surface before they react, whereas on the Cu(111) surface undesired thermal decomposition is observed after annealing at temperatures too low for imine formation.

1) Science 2011, 333, 999; 2) Chem. Sci. 2014, 5, 2789.

O 3.3 Mon 11:00 MA 005

**Potassium doping of ultrathin layers of coronene on Ag(111)** — ●TOBIAS HUEMPFNER, FALKO SOJKA, ROMAN FORKER, and TORSTEN FRITZ — Friedrich Schiller University, Institute of Solid State Physics, Helmoltzweg 5, 07743 Jena, Germany

We report on the influence of potassium doping on ultrathin coronene layers in the (sub-) monolayer regime on Ag(111). The film growth and doping are successively traced in situ via differential reflectance spectroscopy (DRS) [1,2]. During the doping process the formation of a primary phase and, subsequently, of monoanions and dianions was observed by comparing the measured data to solution spectra [3]. After stopping the potassium deposition the dianions decay into monoanions and into molecules in the primary phase. The two latter species are stable and could be further investigated structurally and electronically via low energy electron diffraction (LEED) and scanning tunneling microscopy / spectroscopy (STM, STS). Besides the already known structure for one monolayer (ML) of undoped coronene on Ag(111) a new epitaxial structure is found for a coverage below 1 ML. Although the

doped molecules do not show any highly ordered structure, they could be identified via STM measurements. While the potassium atoms are not resolved in the STM images, the doping process is evidenced by characteristic features in the related STS data.

References: [1] R. Forker *et al.*, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **108**, 34-68 (2012). [2] R. Forker and T. Fritz, Phys. Chem. Chem. Phys. **11**, 2142-2155 (2009). [3] G. J. Hoijtink, Mol. Phys. **2**, 85-95 (1959).

O 3.4 Mon 11:15 MA 005

**STM study of molecular n-dopants for organic electronics** — ●JUSTUS KRÜGER<sup>1,2</sup>, FRANK EISENHUT<sup>1,2</sup>, JÖRG MEYER<sup>1,2</sup>, ANJA NICKEL<sup>1,2</sup>, GIANAURELIO CUNIBERTI<sup>1,2</sup> und FRANCESCA MORESCO<sup>1,2</sup> — <sup>1</sup>Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany — <sup>2</sup>Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

Controllable doping of organic semiconductors is of paramount importance for future application of organic electronics; however, effective air-stable and solution-processable n-type dopants are still rare. A new class of molecular materials based on 1H-benzimidazole derivatives has recently been identified [1] as promising candidate for strong n-type doping. Whereas the experimental results look encouraging, there is still a lack of knowledge on the detailed doping mechanism. Therefore, we have investigated the properties of one particular dopant on a single molecular level by scanning tunneling microscopy (STM) at low temperatures. By depositing dopant and C60 molecules on the same Au(111) surface, the electronic and structural interactions of the host-guest system can be addressed. In particular, spectroscopic measurements of dopant molecules resting on C60 clusters will help to understand the working mechanism of the doping effect. [1] P. Wei *et al.*, J. Am. Chem. Soc. 2010 132 (26), 8852-8853

O 3.5 Mon 11:30 MA 005

**Single photon emission in STM-induced luminescence from fullerene excitons** — ●PABLO MERINO<sup>1</sup>, CHRISTOPH GROSSE<sup>1</sup>, KLAUS KUHNKE<sup>1</sup>, and KLAUS KERN<sup>1,2</sup> — <sup>1</sup>Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany — <sup>2</sup>Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Quantum systems like molecules or quantum dots cannot emit two photons at the same time which results in an antibunching of the emitted photon train and a dip in the photon-photon correlation function. Such single photon emitters are key elements for quantum cryptography and their miniaturization to the nanoscale would be desirable. This requires reproducible emitter separations typically below the optical diffraction limit and has imposed strong limitations on suitable structures and materials. In this contribution we demonstrate single photon emission excited locally by a low temperature (4 K) Scanning Tunneling Microscope (STM) and characterized with sub-molecular resolution. Using a Hanbury Brown-Twiss interferometer scheme in STM-induced electroluminescence we discovered that localized trap states in fullerene multilayers form single photon emitters. The emission spectrum is a line spectrum attributable to exciton recombination and from the correlation data, exciton life times as short as 0.25 ns are determined. With increasing tunnel current a saturation of the emission and a change of the correlation function are observed. We will discuss these observations within the frame of a three state kinetic model.

O 3.6 Mon 11:45 MA 005

**2D-Nanopatterns of molecular polygons and spoked wheels** — ●STEFAN-SVEN JESTER, A. VIKAS AGGARWAL, ROBERT MAY, and SIGURD HÖGER — Rheinische Friedrich-Wilhelms-Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Shape-persistent macrocycles self-assemble at the solid/liquid interface of graphite (HOPG) into two-dimensional monolayer patterns that can be imaged by scanning tunneling microscopy (STM). We recently investigated monolayers of arylene-alkynylene macrocycles that can be viewed as molecular polygons consisting of  $n$  corners and  $n$  sides ( $n = 3 - 6$ ) and form supramolecular Archimedean tiling patterns. Thereby, two conformers of the hexamer were observed: an equilateral

and a collapsed hexagon. Stimulated by these observations, we studied the mono- and multilayer formation of molecular spoked wheels, in which the hexagonal macrocycle rim is stiffened by an intraannular spoke/hub system. In addition, the importance and informative value of STM techniques for the compound characterization of large organic molecules is highlighted. [1] S.-S. Jester, E. Sigmund, S. Höger *J. Am. Chem. Soc.* **2011**, *133*, 11062. [2] S.-S. Jester, A. V. Aggarwal, D. Kalle, S. Höger *Beilstein J. Org. Chem.* **2014**, *10*, 2783. [3] R. May, S.-S. Jester, S. Höger *J. Am. Chem. Soc.* **2014**, DOI: 10.1021/ja5096705.

O 3.7 Mon 12:00 MA 005

**Polymer statistics of single P3HT molecules on Au(001) determined by STM** — ●ERIK KOHL<sup>1</sup>, STEFAN FÖRSTER<sup>1</sup>, and WOLF WIDDRA<sup>1,2</sup> — <sup>1</sup>Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — <sup>2</sup>Max-Planck-Institute für Mikrostrukturphysik, Halle, Germany

Using in-situ UHV electrospray deposition (ESD), isolated poly(3-hexylthiophene) (P3HT) molecules have been deposited on a Au(001) surface. Scanning tunneling microscopy (STM) reveals two different adsorption states of P3HT in the low coverage limit at room temperature: Strongly adsorbed polymer chains show fully stretched conformations, which result from a reorganization of the surface atoms in the presence of the polymer chain [1]. Additionally, weakly adsorbed molecules are present, which show two-dimensional random-coil like conformations.

For the weakly adsorbed P3HT species, the full statistical information is extracted from STM measurements. By tracing the experimentally observed chain configurations, the radius of gyration and the end-to-end distance of about 700 molecules of different polymer lengths have been extracted in the single chain limit [2].

[1] S. Förster and W. Widdra, *J. Chem. Phys.* **141**, 054713 (2014)

[2] S. Förster, E. Kohl, M. Ivanov, J. Gross, W. Widdra and W. Janke, *J. Chem. Phys.* **141**, 164701 (2014)

O 3.8 Mon 12:15 MA 005

**Thermally and photoinduced polymerization of ultrathin sexithiophene films** — ●ANKE SANDER<sup>1,3</sup>, RENE HAMMER<sup>1</sup>, KLAUS DUNCKER<sup>1</sup>, STEFAN FÖRSTER<sup>1</sup>, and WOLF WIDDRA<sup>1,2</sup> — <sup>1</sup>Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — <sup>2</sup>Max Planck Institute of Microstructure Physics, Halle, Germany — <sup>3</sup>present address: Unite Mixte de Physique CNRS/Thales, Palaiseau, France

Due to their semiconducting properties, polythiophenes are highly promising for use in organic electronics. Apart from their direct deposition onto a substrate, one could also deposit smaller thiophene compounds and form covalent bonds between them by further processing which additionally enables a manipulation of the morphology. This study addresses the polymerization of ultrathin sexithiophene (6T) films on Ag(001) and Au(001). Annealing of initially well-ordered films leads to local reactions between neighboring molecules. Depending on the surface temperature and the annealing time, long unbranched polythiophene polymers or branched polymer networks are formed. In general, the onset temperature and the complexity of structure formation depend on the strength of interaction with the underlying substrate. Here, on both substrates the polymerization occurs at temperatures significantly lower than found for crystalline powder. Similar structural changes and 6T polymerization are found upon ex-

posure to UV radiation in the range from 3.0 to 4.2 eV. The observed reactions induced by thermal annealing as well as by UV excitation are explained by a polymerization via formation of cation radicals that necessitates the interplay with metallic substrate states.

O 3.9 Mon 12:30 MA 005

**Layer resolved evolution of  $\alpha$ -sexithiophene films: Correlation between PEEM and optical reflectance** — ●EBRAHIM GHANBARI, THORSTEN WAGNER, and PETER ZEPPEFELD — ebrahim.ghanbari@jku.at

$\alpha$ -sexithiophene ( $\alpha$ -6T) is a well-known organic dye pigment which represents a model system to study the photo-physical properties of  $\pi$ -conjugated molecules. We apply a combination of Differential Reflectance Spectroscopy (DRS) and Photo Electron Emission Microscopy (PEEM) to follow the growth of  $\alpha$ -6T on Ag(111) surfaces in real time. The deposition of the molecules modifies the density of states at the surface as well as the actual photoelectron emission barrier. Therefore, the lateral variation of the electron yield can be used to follow the growth of layers and 3D crystallites. Initially, the PEEM intensity rises uniformly across the entire field of view (145  $\mu\text{m}$ ) until the first layer is closed. The following drop of the electron yield is terminated when the wetting layer is completed and the nucleation of 3D islands sets in. The initial rise of the electron yield can be attributed to the formation of an interface dipole. The DRS and the PEEM measurements are synchronized and both signals are recorded simultaneously. The evolution of different features in the normalized differential optical reflectance can be attributed to the formation of the first layer, the second layer, as well as the nucleation and growth of 3D crystallites. Thus, we obtain a direct correlation between the PEEM and the transients of the spectral reflectance which provides a deeper insight into the nature of the adsorbate-metal system.

O 3.10 Mon 12:45 MA 005

**Structural, optical, and electronic properties of mono- and multilayers of tetraphenyldibenzoperiflanthene (DBP)** — ●TINO KIRCHHUEBEL<sup>1</sup>, TINO MORGENROTH<sup>1</sup>, MARCO GRUENEWALD<sup>1</sup>, ROMAN FORKER<sup>1</sup>, TAKASHI YAMADA<sup>2</sup>, TOSHIKI MUNAKATA<sup>2</sup>, FABIO BUSSOLOTTI<sup>3</sup>, SATOSHI KERA<sup>3</sup>, NOBUO UENO<sup>3</sup>, and TORSTEN FRITZ<sup>1</sup> — <sup>1</sup>Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany — <sup>2</sup>Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan — <sup>3</sup>Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

The dye molecule tetraphenyldibenzoperiflanthene (DBP,  $\text{C}_{64}\text{H}_{36}$ ) [1] is a promising candidate for usage in opto-electronic devices. It consists of an aromatic backbone and four additional phenyl rings perpendicular to the molecular plane. In order to investigate the growth and the optical properties of DBP on various substrates from submonolayers to 10 monolayers, in situ differential reflectance spectroscopy (DRS) [2,3] measurements were performed. A strong interaction between molecules and single crystalline metal surfaces was found, where structural characterization by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) at cryogenic temperatures revealed a well-ordered flat-lying thin film growth in a herringbone arrangement in the first monolayer. Depending on the coverage two distinct spectral fingerprints of DBP molecules could be identified for multilayer films. To elucidate their origin, complementary photoelectron spectroscopies as well as (time dependent) density functional theory ((TD-)DFT) calculations were performed.