O 12: Organic Molecules at Surfaces 2: Characterization of Organic Monolayers

Time: Monday 15:00–18:00 Location: S051

O 12.1 Mon 15:00 S051

Quantifying Interactions in Organic Monolayers — •Pierre-Martin Dombrowski, Stefan Renato Kachel, Leonard Neuhaus, Tobias Breuer, J. Michael Gottfried, and Gregor Witte — Philipps-Universität Marburg, Germany

The formation of molecular nanostructures is determined by the interplay of intermolecular and molecule-substrate interactions, whose experimental determination is challenging. Temperature-programmed desorption (TPD) is a well-established technique capable of quantifying these interactions, but its analysis is by no means trivial and therefore rarely done quantitatively for large adsorbates. In the present study, we analyse the desorption kinetics of the two organic semiconductors pentacene and perfluoropentacene from Au(111) and MoS_2 surfaces to show the potential of TPD and highlight challenges for larger adsorbates. [1,2] Combining TPD with scanning tunnelling microscopy, work function measurements and theoretical modelling, we show that intermolecular interactions are dominated by the intramolecular charge distribution. We are further able to determine the coverage-dependent prefactor of desorption with unprecedented precision, which enables a correlation of the desorption signal with the activation of specific degrees of freedom of motion of adsorbed molecules. Lastly, we compare the differences in molecule-substrate interactions for the two substrates at hand, which reveals that entropy can stabilize organic monolayer films on MoS_2 despite a weak molecule-substrate bond.

[1] S. R. Kachel et al., *Chem. Sci.* (2021), **12**, 2575-2585.

[2] P.-M. Dombrowski et al., *Nanoscale* (2021), **13**, 13816-13826.

O 12.2 Mon 15:15 S051

Toward Understanding Thermal and Electric Properties of Single Molecular Junctions and Self-Assembled Monolayers — •Mohamed Ibrahim[1], Philipp Wiesener[1], Luke O'Driscoll[2], Martin Bryce[2], and Achim Kittel[1] — [1]Oldenburg University, Oldenburg, Germany — [2]Durham University, Durham, England

Over the last years, implanting organic molecules in devices is continuously attracting large attention because of their small size (nm scale), tunable electronic and thermal properties by manipulating individual atoms. Therefore, it is obvious to extend the field of thermoelectrics using molecules to cool devices and sensors very locally. A single layer of well organized molecules is formed and realized by the self assembly mechanism, which allows molecular moieties to be adsorbed spontaneously on a surface producing large domains. This motivated us to report here about the characterisation of selfassembled oligo phenylene ethynylene dithiol molecules (OPE3), and some specifically modified forms by mainly adding side groups to it on gold surfaces by means of X-ray photoelectron spectroscopy (XPS), reflected electron energy loss (REELS), and ultraviolet photoelectron spectroscopy (UPS). The results show that the unsubstituted OPE3 has a high densely packed SAM with a thickness 1.7 nm, while the presence of substituents, attached to the middle ring, led to variation of the SAM film thickness. This indicates changes in the geometric configuration of the π stacking of OPE3 especially, tilt angle and packing densities. Parent OPE3 REELS spectrum shows a band gap value of 2.01 eV which is totally different than the reported value in the literature.

O 12.3 Mon 15:30 S051

Molecular orientation and phase transitions of DHTAP — •Claudia López-Posadas[1], Michael Györök[1], Antony Thomas[2], Thomas Leoni[2], Olivier Siri[2], Conrad Becker[2], and Peter Zeppenfeld[1] — [1]Institute of Experimental Physics, Johannes Kepler University Linz, Altenberger Str. 69, 4040 Linz, Austria — [2]Aix-Marseille University, CNRS, CINaM, UMR 7325, F-13288 Marseille, France

The structure and orientation of 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAP) layers deposited on Cu(110), Cu(110)-(2x1)O and the Cu(110)/Cu(110)-(2x1)O stripe phase was studied using reflectance difference spectroscopy (RDS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). The evolution of the RDS signal allows to identify the sequential formation of up to three monolayers as well as a phase transition upon completion of the first one. On Cu(110), DHTAP molecules in the first monolayer are always lying flat with their long molecular axis aligned parallel to the [-110]-direction of the Cu(110) surface. However, for subsequent layers the orientation critically depends on the deposition temperature T. At T=240K the DHTAP molecules are mostly aligned parallel to the ones in the first layer, whereas at room temperature and above their preferential orientation is orthogonal to the molecules in the first layer, the coexistence of the two orientations can be observed at a critical temperature of T=270K. Finally, the main optical transitions and the orientation of the transition dipole moments of the DHTAP layers were extracted from the RDS spectra.

O 12.4 Mon 15:45 S051

Nickel(II) Porphyrins on Metal Surfaces: Oxidation-State Tuning and Formation of a Supramolecular Mixed-Valence Adsorbate Structure — •Jan Herritsch, Qitang Fan, Marie-Irène Albus, Lukas Ruppenthal, Lukas J. Heuplick, Leonard Neuhaus, Tobias Wassermann, and J. Michael Gottfried — Philipps-Universität Marburg

Nickel tetrapyrrole complexes are structurally related to biologically relevant molecules (e.g., F430 cofactor, tunichlorin, nibalamine) and are promising precursors for novel functional interfaces. Here, we report on the influence of the interaction at the metal/organic interface on the electronic structure of a nickel octaethyl porphyrin (Ni(OEP)) monolayer on different coinage metal surfaces studied by XPS, UPS, STM, NEXAFS and LEED. On Ag(111), Ni(OEP) forms a mixed-valent adsorbate phase in which the Ni centers occur in two different oxidation states. The two separate peaks in the Ni 2p XP spectrum indicate that about 40% of the Ni centers are reduced. STM and LEED show an incommensurate superstructure with an ordered arrangement of the metal centers in different oxidation states. Further insights into the valence electronic structure were obtained by UPS and NEXAFS. On the more reactive Cu(111) surface, Ni(OEP) forms a long-range ordered structure in which nickel centers are uniformly reduced; whereas on the most inert Au(111) surface, the oxidation state of the Ni centers remains unaffected by adsorbate interactions.

O 12.5 Mon 16:00 S051

Electronic and structural properties at the NiTPP/O-Cu(100) interface — •Jonah Elias Nitschke[1], Henning Sturmeit[1], Iulia Cojocariu[2], Vitaliy Feyer[2], Alessandro Sala[2], Andreas Windischbacher[3], Peter Puschnig[3], Stefano Ponzoni[1], Giovanni Zamborlini[1], and Mirko Cinchetti[1] — [1]Department of Physics, TU Dortmund University, Germany — [2]Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, Germany — [3]Institute of Physics, University of Graz, Austria

Depending on the strength of the molecule-substrate interaction, charge transfer, chemical reactions or a redistribution of the electronic cloud may occur at organic-metal interfaces. Here, we investigate the structural and electronic properties of Nickel tetraphenylporphyrin molecules (NiTPP) deposited on oxygen-passivated Cu (100) surface. By using a multi-technique approach, which combines LEED and STM, we reveal a coverage dependent superstructure with multiple domains that ultimately reduces into a single unit cell.

In the latter configuration, STM measurements show that the NiTPP molecules adsorb either with the macrocycle planar to the surface on in a saddle-shape configuration, with the pairs of opposite pyrrole rings tilted upwards. STS and photoemission orbital tomo-graphy measurements show that, contrary to the NiTPP adsorbed on the bare Cu(100) surface, where a significant charge transfer is observed, the oxygen overlayer quenches the charge transfer at the interface, thus offering a simple approach to physically decouple of the molecular film from the underlying substrate.

O 12.6 Mon 16:15 S051

Surface Chemical Bond and Molecular Topology of Polycyclic Aromatic Systems — •Lukas Ruppenthal[1], Florian Münster[1], Benedikt P. Klein[1], Jan Herritsch[1], Leonard Neuhaus[1], Stefan R. Kachel[1], Pengcai Liu[2], Xing-Yu Chen[2], Jiawen Cao[2], Lars E. Sattler[3], Sebastian M. Weber[3], Qitang Fan[1], Gerhard Hilt[3], Xiao-Ye Wang[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, Philipps-University Marburg, Germany — [2]College of Chemistry, Nankai University Tianjin, China — [3]Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany

Metal/organic interfaces have a large impact on the performance of organic (opto-)electronic devices. Therefore, the detailed understanding of their chemical, electronic and geometric structure is important for the further technological development. Many common organic semiconductors contain π-electron systems with alternant topologies, whereas non-alternant alternatives have only recently found increasing attention due to their unusual electronic properties. Here, we compare the alternant polycyclic aromatic molecule pyrene with its non-alternant isomers acepleiadylene and azupyrene regarding their interaction with Cu(111) surface, using PES, NEXAFS, TPD and STM. The non-alternant isomers are also interesting as molecular models of graphene defects, e.g. azupyrene for the Stone-Wales defects. In all cases, the non-alternant isomers show increased metal/molecule-interaction due to their reduced HOMO-LUMO gap, which brings the LUMO energetically closer to the Fermi energy of the metal, causing stronger hybridization with electronic states of the metal surfaces.

O 12.7 Mon 16:30 S051

Tailoring the organic-semiconductor/metallic interface: From self-assembly to heteromolecular phases of carboxylic acids on Ag surfaces — •Matthias Blatnik, Veronika Stará, Anton Makoveev, Jakub Planer, Thomáš Krajňak, Pavel Procházka, and Jan Čechal — CEITEC BUT, Brno, CZ

Atomic-level understanding of the metal/organic-semiconductor interface has become paramount in the strife for the development and fabrication of more efficient organic electronic devices in recent years. Interfacial properties are crucially linked to molecule-molecule and molecule-substrate interactions, molecular functionalization (e.g., deprotonation), a precise energy level alignment, substrate termination or the formation of multi- or heterolayers with a different organic compound. All these have to be well understood through the study of model systems in ultra-clean conditions before technological advances can be achieved. Here, we present a model system of self-assembled aromatic carboxylic acids (e.g., 4,4' Biphenyl Dicarboxylic Acid, 1,3,5-Benzenetribenzoic Acid) on Ag surfaces (orientations (100) and (111)). We explore the effects of the metal substrate's orientation on formation and growth of single molecular phases, introduce a monolayer thick layer as a charge injection layer and study the formation of a heteromolecular compound with an additional organic material (e.g., pentacene). We employ low energy electron microscopy (LEEM) and diffraction (μLEED), as well as STM and XPS to give a real-time view and detailed information on nucleation and growth of the molecular phases and transformations and the chemical composition.

O 12.8 Mon 16:45 S051

Highly ordered commensurate structures of merocyanines on Ag(100) — •Anna Juliana Kny[1], Max Reimer[2], Noah Al-Shamery[1], Ritu Tomar[1], Thomas Bredow[1], Selina Olthof[2], and Moritz Sokolowski[1] — [1]Institut für Physikalische und Theoretische Chemie der Universität Bonn, Germany — [2]Department für Chemie der Universität zu Köln, Germany

Vacuum deposited films of the merocyanine molecule 2-[5-(5-dibutylamino-thiophen-2-yl-methylene)-4-*tert*-butyl-5*H*-thiazol-2-ylidene]-malononitrile (HB238) and its derivatives have been investigated in the context of organic solar cells [1].

Although the specific structural order in these films is important for the optical properties, only very little is known about the adsorption and ordering of merocyanines on surfaces. Therefore, we investigated monolayers of HB238 on a Ag(100) surface by SPA-LEED, STM, XPS, UPS, and DFT calculations.

Upon deposition onto the Ag(100) surface at room temperature the formation of a commensurate superstructure is observed. It is composed of homochiral HB238 aggregates of four molecules. We discuss the surface bonding and structure formation in dependence of the specific functional groups and, furthermore, the sterically demanding donor substituents. For the role of the latter one, we also investigated derivatives of HB238 on Ag(100). The merocyanines were synthesized and kindly provided by the group of Prof. K. Meerholz (Cologne).

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O 12.9 Mon 17:00 S051

Van der Waals Heteroepitaxy: Intrinsic Epitaxial Alignment of Perfluoropentacene Films on Transition Metal Dichalcogenides — •Maximilian Dreher, Darius Günder, and Gregor Witte — Philipps-University Marburg, Germany

In this work, we have studied the formation and azimuthal alignment of crystalline adlayers of the organic semiconductor (OSC) perfluoropentacene (PFP) on the basal plane of several transition metal dichalcogenides (TMDC) single crystals, which are further compared to graphite and hBN. The quite inert basal planes of TMDCs enable an unrestricted growth of OSCs without the requirement of relaxation in terms of commensurability at the interface, since molecules exhibit a stronger interaction among each other than with the substrate. Nevertheless, the crystalline PFP multilayers exhibit distinct azimuthal twist angles relative to the substrate surface, which we could rationalize by so called 'on-line coincidences' introduced by Forker et al. recently. [1] Here, the molecules do not favor a specific adsorption site at the interface as it is often described by commensurate superstructures. Instead the bulk crystal structure remains unperturbed down to the interface, but a specific twist angle is adopted, where molecules avoid unfavored adsorption sites. The extreme sensitivity of the resulting twist angles by small deviations in the crystal structure enabled us further to use the large thermal expansion of the OSC to control the twist angles by changing the substrate temperature during deposition. [1] Forker et al., Soft Matter 13, 1748-1758 (2017) [2] Dreher et al., Chem. Mater. 32, 20, 9034-9043 (2020)

O 12.10 Mon 17:15 S051

Steering Self-Assembly of Three-Dimensional Iptycenes on Au(111) by Tuning Molecule-Surface Interactions — Lukas Grossmann[1,2], •Eva Ringel[1,2], Wolfgang Heckl[1,2], and Markus Lackinger[1,2] — [1]Deutsches Museum, Museumsinsel 1, 80538 München — [2]Technische Universität München, Physics Department, James-Franck-Strasse 1, 85748 Garching

Three-dimensional organic molecules have been neglected in studies on surfaces, even though their self-assemblies exhibit a far greater variability than their planar counterparts. While planar molecules adsorb mostly flat on surfaces, three-dimensional molecules can adopt vastly different adsorption geometries. This additional degree of freedom can result in self-assembly of entirely different supramolecular structures. Moreover, adsorption geometries can be steered by tuning molecule-surface interactions, thereby providing a new means for 2D crystal engineering. In this respect, iptycenes are highly stable, but currently underexplored model compounds. Here, we study self-assembly of threefold symmetric triptycene derivates with extended anthracene blades on Au(111) surfaces. Additionally, the influence of intrinsic dipole moments was investigated by comparing analogs with peripheral fluorine substitution. All structures were resolved by Scanning-Tunneling-Microscopy under ultra-high vacuum conditions. On pristine Au(111), the molecules maximize the area of contact, whereas iodine-passivation affords hexagonal porous structures that feature optimized molecule-molecule interactions through face-to-face stacking of all anthracene blades.

O 12.11 Mon 17:30 S051

Adsorption of Submonolayer Coverages of Phenylphosphonic Acid on Rutile TiO2(110) — •Alexander Wolfram[1], Maximilian Muth[1], Julia Köbl[1], Nataliya Tsud[2], Sascha Mehl[3], Hans-Peter Steinrück[1], and Ole Lytken[1] — [1]Friedrich-Alexander Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie 2, Egerlandstr. 3, 91058 Erlangen, GER — [2]Charles University, Faculty, of Mathematics and Physics, Department of Surface and Plasma Science, Holešovičkách 2, Prague, 18000, Czech Republic — [3]Elettra-Sincrotrone Trieste SCpA, Strada Statale 14, km 163.5, Trieste, Basovizza, 34149, Italy

The interfaces of oxide surfaces with organic molecules are crucial for the performance of devices, such as dye-sensitized solar cells, sensors and organic electronics. All these devices contain interfaces where organic molecules are bound to surfaces, often using covalent anchoring groups. These anchoring groups strongly influence the interface and thus the device performance. An interesting anchoring group is the phosphonic acid group, which is well known to bind strongly to oxide surfaces. At ELETTRA sinchrotrone in Trieste we investigated submonolayer coverages of phenylphosphonic acid on a rutile TiO_2 (110) surface with high-resolution X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Based on the changes in the O 1s and P 2p core levels, we are able to identify the different binding motifs present on the surface at different temperatures, while the NEXAFS intensities gives us information about the orientation of the phenyl moiety.

O 12.12 Mon 17:45 S051

Accurate determination of adsorption-energy differences of metalloporphyrins on TiO2(110) 1x1 — •Maximilian Muth,

Alexander Wolfram, Elmar Kataev, Julia Köbl, Hans-Peter Steinrück, and Ole Lytken — Univ. Erlangen-Nürnberg

A deeper knowledge of the behavior between porphyrin molecules and the rutile TiO2(110) surface and is of crucial importance for the development of new applications. Especially the usage of such systems in photocatalysis or solar cells are promising possibilities. Therefore, we investigated the adsorption energy of three different metallo-tetraphenylporphyrins (MTPP M = Mg, Co, Zn). Unfortunately, temperature programmed desorption, a typical method for the determination of adsorption energies is not applicable for this particular system because of the irreversible adsorption of the monolayer in direct contact to the TiO2-surface. For this reason, instead, we compared the adsorption-energy of the three MTPPs relatively to each other by using a layer exchange experiment. We adsorb mixtures of always two different MTPPs on top of each other and allow the molecules to diffuse during a heating ramp. Eventually, an equilibrium state forms in which the MTPP with the higher adsorption-energy will enrich in the monolayer in direct contact with surface while the weaker adsorbing MTPP will be enriched in the multilayer. After further heating for multilayer desorption we determine the concentrations of the MTPPs found in the remaining monolayer by using XPS and use them to calculate the difference in adsorption-energy of MTPPs via the equilibrium constant.