

O 42: Poster Tuesday: Organic Molecules on Inorganic Surfaces

Time: Tuesday 18:00–20:00

Location: Poster D

O 42.1 Tue 18:00 Poster D

LT-UHV-STM Investigations on Various Supramolecular Structures of Benzyl-naphthoic Diimides Adsorbed on an Au(111)-Surface — ●BERTRAM SCHULZE LAMMERS^{1,2}, RENÉ EBELING², ELENA DIRKSEN³, THOMAS J. J. MÜLLER³, and SILVIA KARTHÄUSER² — ¹Institute of Physics and Center for Nanotechnology, University of Münster, Germany — ²Peter Grünberg Institut (PGI-7) and JARA-FIT, Forschungszentrum Jülich GmbH, Germany — ³Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf, Germany

By means of the LT-UHV-STM technique we investigated 2,7-dibenzyl 1,4,5,8-naphthalenetetracarboxylic diimide (BNTCDI), which consists of a naphthalene diimide (NDI) backbone and two benzyl groups. On a Pt(111)-surface it showed the formation of an effective transport path via hybrid BNTCDI/Pt d-states [1]. For a deeper understanding we investigated BNTCDI on an Au(111)-surface, where a weak physisorption is expected. As a result, we obtained one- and two-dimensional supramolecular structures. Orbital-resolved STM imaging allows us to identify intramolecular hydrogen bonds between the NDI-backbones as the driving force for the one-dimensional arrangements on step-edges. The two-dimensional structures on the terraces emerge as ordered and disordered molecular double layers. Locally resolved STS measurements reveal the characteristic electronic properties of BNTCDI and the influence on these by different substrate coupling strengths. In particular, we identify a LUMO-shift and an edge-state coupling as prominent adsorption driven influences. [1] DOI: 10.1021/acs.jpcc.7b09911

O 42.2 Tue 18:00 Poster D

Metalation of phthalocyanines on semimetal surfaces and the manifestation of interfacial electronic structures — JINBANG HU^{1,2}, ZHENGDE ZHANG¹, KONGCHAO SHEN^{1,3}, ZHAOFENG LIANG^{1,2}, HAOLIANG SUN^{1,2}, JINPIN HU^{1,2}, GENGWU JI¹, XINGYU GAO¹, PING HUAI¹, ZHIYUAN ZHU¹, ZHENG JIANG¹, HAN HUANG⁴, ●FRODE STRAND⁵, RAJESH CHELLAPPAN⁵, JUSTIN WELLS⁵, BO SONG⁶, and FEI SONG¹ — ¹IPAT and SSRF, Shanghai. Institute of Applied Physics, SINAP CAS, Shanghai, China — ²UCAS, Beijing, China — ³Department of Physics, ZHU, Hangzhou, China — ⁴School of Physics and Electronics, CSU, Changsha, China — ⁵Center of Quantum Spintronics and Department of Physics, NTNU, Trondheim, Norway — ⁶USST, Shanghai, China

On-surface engineering of supramolecular structures has attracted much interest during past decades, for example, the manipulation of metal coordination, hydrogen bonding and so on. However, organic nanostructures coordinated by group-V semimetals have generally not been reported. Specifically, synthesis of non-transition metal phthalocyanines (PC) are scarcely discussed in the literature. Here we will report on the on-surface metalation of H2-PC to form Bi-PC (and similarly Sb-PC). The formation of Bi-PC is studied using XPS and LEED, and the interfacial electronic states are studied using UPS. Our findings confirm the feasibility of on-surface metalation of H2PC to form non-transition-metal PCs which are otherwise difficult to synthesise.

O 42.3 Tue 18:00 Poster D

Exciting vibrons in both frontier orbitals of a single hydrocarbon molecule on graphene — ●ALEXANDER MEHLER¹, NICOLAS NÉEL¹, MARIE-LAURE BOCQUET², and JÖRG KRÖGER¹ — ¹Institut für Physik, Technische Universität Ilmenau, Ilmenau, Germany — ²Department of Chemistry, UMR ENS-CNRS-UPMC 8640, Ecole Normale Supérieure, Paris, France

Vibronic excitations in molecules are key to the fundamental understanding of the interaction between vibrational and electronic degrees of freedom. In order to probe the genuine vibronic properties of a molecule even after its adsorption on a surface appropriate buffer layers are of paramount importance. Here, vibrational progression in both molecular frontier orbitals is observed with submolecular resolution on a graphene-covered metal surface using scanning tunnelling spectroscopy. Accompanying calculations demonstrate that the vibrational modes that cause the orbital replica in the progression share the same symmetry as the electronic states they couple to. In addition, the vibrational progression is more pronounced for separated molecules than for molecules embedded in molecular assemblies. The entire vibronic spectra of these molecular species are moreover rigidly shifted

with respect to each other. This work unravels intramolecular changes in the vibronic and electronic structure owing to the efficient reduction of the molecule-metal hybridization by graphene.

O 42.4 Tue 18:00 Poster D

Promoted exchange reaction between alkanethiolate self-assembled monolayers and an azide-bearing substituent — RUI YAN¹, LOÏC LE PLEUX², MARCEL MAYOR^{2,3}, and ●MICHAEL ZHARNIKOV¹ — ¹Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — ²University of Basel, Department of Chemistry, CH-4056 Basel, Switzerland — ³Forschungszentrum Karlsruhe GmbH, Institute for Nanotechnology, 76021 Karlsruhe, Germany

The possibility of ultraviolet-light-promoted exchange reaction between the primary alkanethiolate (AT) self-assembled monolayers (SAM) and an azide-functionalized substituent (12-Azido-1-dodecanethiol, C12N3), capable of click reaction with ethynyl-bearing species, is demonstrated. This reaction resulted in the mixed AT/C12N3 films, with the portion of C12N3 precisely controlled by selection of a suitable UV dose. As the primary matrix, either non-substituted or oligo(ethylene glycole) (OEG) substituted AT SAMs were used, targeting mixed SAMs of chemical and biological significance. The surface density of the chemically active azide groups embedded in the non-reactive primary matrix could be precisely varied. For the OEG-AT/C12N3 films, this resulted in the preparation of templates for specific protein adsorption, comprising biotin-bearing moieties embedded in the protein-repelling OEG-AT matrix. The entire approach was extended to lithography, relying on a commercial maskless UV lithography setup.

O 42.5 Tue 18:00 Poster D

Revealing spectroscopic signatures of molecule-metal interaction: A computational core-level spectroscopy study — ●SAMUEL J. HALL and REINHARD J. MAURER — Department of Chemistry, University of Warwick, Coventry, United Kingdom

Core-level spectroscopy, both x-ray absorption (XAS) and photoemission (XPS), represents an immensely important tool for the characterisation of complex hybrid organic-inorganic interfaces. The information on these interactions is often hidden in a convolution of spectroscopic signatures that is affected by initial state effects (e.g. chemical bonding) and final state effects (e.g. molecule-metal charge-transfer and hybridisation) alike. First-principles simulation of core-level spectra enables us to disentangle these effects and offers a systematic assessment of varying molecule-metal interaction strength and its spectral manifestation. On the examples of small conjugated organic molecules and aromatic carbon nanostructures at single-crystal metal surfaces such as Cu(111), Ag(111), and Pt(111), we investigate the signatures of molecule-metal bonding by simulating near-edge X-ray absorption fine-structure (NEXAFS) and XPS spectra. Calculations were carried out using dispersion-inclusive Density Functional Theory calculations using the transition potential method. [1,2] Using orbital-projection techniques, we are able to provide a full spectral decomposition in terms of initial and final states. In combination with a charge and structure analysis, we arrive at a detailed picture of how molecular composition and metal reactivity affect core-level spectra. [1] JCP **146**, 214701 (2017), [2] PRB **58**, 8097 (1998)

O 42.6 Tue 18:00 Poster D

Electronic Structure of decoupled molecules: 1,2,8,9-dibenzopentacene on h-BN on Pt(111) — ●MAXIMILIAN SCHAAL, FELIX OTTO, BERND SCHRÖTER, ROMAN FORKER, and TORSTEN FRITZ — Friedrich Schiller University Jena, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena

The strong hybridisation of molecules on metal single crystals causes a strong change of the structural and electronic properties. Insulating interlayers like 2D hexagonal boron nitride (h-BN) can be used to study the undisturbed properties of decoupled molecular layers. For this purpose we studied the change of the electronic structure of 1,2,8,9-dibenzopentacene (trans-DBPen) molecules upon adsorption on h-BN/Pt(111). The h-BN monolayer was grown by thermal dehydrogenation of borazine on Pt(111). The layer quality was determined by x-ray photoelectron diffraction (XPD) and low energy electron diffraction (LEED). The thickness of the trans-DBPen layer

was controlled by in-situ differential reflectance spectroscopy (DRS). The electronic structure of this organic-inorganic heterostructure was observed with ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) and compared to the electronic structure of bare h-BN on Pt(111) and trans-DBPen directly on Pt(111). By measuring the band structure it was possible to identify several molecular states. Furthermore, the highest occupied molecular orbital (HOMO) was investigated by measuring the photoelectron momentum maps (PMMs). Finally the results show the desired effect of decoupled trans-DBPen molecules on h-BN/Pt(111).

O 42.7 Tue 18:00 Poster D

Understanding the Mechanism of Metalation at Porphyrin/CoO(111) Interfaces with Photoemission Spectroscopy — ●CAN WANG, RUIMEI WANG, and THOMAS FAUSTER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Understanding the electronic structure between porphyrins and metal oxide interfaces is vital for the rational design of functional molecular architectures [1, 2]. Well-ordered thin layers (~ 5 ML) of rock-salt structure CoO(111) are epitaxially grown on Ir(100) [3, 4]. Here, we study the electronic properties of porphyrin (2H-DPP and 2H-TPP) films adsorbed on CoO(111) surface by means of photoemission spectroscopy methods. We observed the direct metalation between porphyrin molecules (~ 1 ML) and CoO(111) interface at room temperature with N 1s core-level shifts obtained by using XPS measurements. The formation of Co-DPP or Co-TPP lead an additional electronic state located ~ 0.4 eV below the Fermi level in UPS spectrum. The UV photoemission data, obtained from monolayer films of 2H-DPP and 2H-TPP also show a large decrease of work function.

[1] W. Auwärter et al., Nat. Chem. 7, (2015) 105.

[2] G. Di Filippo et al., J. Chem. Phys. 146, (2017) 064702.

[3] K. Heinz et al., J. Phys.: Condens. Matter 25, (2013) 173001.

[4] S. Otto and Th. Fauster, J. Phys.: Condens. Matter 28, (2016) 055001.

O 42.8 Tue 18:00 Poster D

Influence of Porphyrinoid Ring Contraction: Transition Metal Corroles — ●JAN HERRITSCH¹, JAN-NICLAS LUY¹, MALTE ZUGERMEIER¹, FALK NIEFIND¹, QITANG FAN¹, MARTIN SCHMID¹, PETER SCHWEYEN², MARTIN BRÖRING², RALF TONNER¹, and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²Institut für Anorganische und Analytische Chemie, TU Braunschweig, Germany

Porphyrin complexes are well studied model systems for surface functionalization. Their reactivity can be controlled by variation of the ligand skeletal structure and the central atom. The related corroles represent contracted porphyrins. Contrary to the formally dianionic porphyrins, they usually act as trianionic ligands and stabilize higher oxidation states of the central atom. Here, we present the on-surface synthesis and characterization of different transition metal corroles (Fe, Co, Ni) on the Ag(111) surface and compare them with the corresponding porphyrins. Thus, we have studied the influence of ring contraction on the electronic structure and adsorbate-substrate interactions. The electronic states of the cobalt and nickel corrole complexes were found to be very similar to those of the corresponding porphyrins. This can partly be explained by the redox non-innocent behavior of the corrole ligand. In case of iron the corrole and porphyrin complexes differ from each other in their electronic state according to XP and NEXAFS spectra. These findings can be observed in the substrate-decoupled multilayer as well as in the monolayer and a higher oxidation state of the iron corrole was verified by UPS.

O 42.9 Tue 18:00 Poster D

Surface Chemical Bond of Alternant vs. Non-Alternant Aromatic Isomers — ●RUPPENTHAL LUKAS, BENEDIKT P. KLEIN, JAN HERRITSCH, STEFAN R. KACHEL, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Germany

Metal/organic interfaces have a large impact on the performance of organic-electronic devices. The detailed understanding of their chemical, electronic and geometric structure is therefore important for the further technological development. Many common organic semiconductors contain aromatic structures with alternant topologies, whereas non-alternant alternatives have found far less interest. Here, we compare naphthalene as an alternant aromatic molecule to azulene as its non-alternant isomer, both on Cu(111), using PES, NEXAFS, TPD, STM, and LEED. With the same approach, we compare the larger aromatic compounds pyrene and its isomer dicyclopenta[*ef,kl*]heptalene (azupyrene), which is also important as a model for the STONE-WALES defects in graphene. Related studies on organometallic sandwich complexes include bis(benzene)chromium and the corresponding non-alternant cyclopentadienyl-cycloheptatrienyl-chromium. In all cases, we find that the non-alternant structure forms a stronger bond to the metal surface than its alternant counterpart. The main reason for this is that the non-alternant species have a smaller HOMO-LUMO gap, which makes them both better donors and better acceptors compared to the alternant species. The resulting effects on the electronic and geometric structure will be discussed on the basis of DFT calculations.

O 42.10 Tue 18:00 Poster D

Orbital Imaging of Pentacene Bilayers on Ag(110) — ●KIANA BAUMGÄRTNER¹, MANUEL GRIMM¹, CHRISTIAN METZGER¹, MARTIN GRAUS¹, MATTEO JUGOVAC², GIOVANNI ZAMBORLINI², VITALIY FEYER², ACHIM SCHÖLL¹, and FRIEDRICH REINERT¹ — ¹Julius-Maximilians-Universität Würzburg, Experimental Physics VII, 97074 Würzburg, Germany — ²Forschungszentrum Jülich GmbH, Peter Grünberg Institut (PGI-6), 52425 Jülich, Germany

Pentacene, a planar organic molecule being widely used in organic electronic devices, is known to form well-ordered single layers when evaporated atop Ag(110). Due to substrate-molecule interactions, the molecules of the first layer will align themselves flat-lying and commensurately along the [001] direction of the substrate. When adding a second layer of molecules, the orientation of growth is increasingly determined by intermolecular forces resulting in a tilt angle of the first layer away from the substrate surface and an even larger tilt angle in the second layer. To evaluate the exact angles of the individual layers, photoelectron momentum maps were recorded with a photoemission electron microscope in k-space imaging mode (kPEEM) at a synchrotron radiation source. The obtained momentum maps contain information on the orientation of the investigated orbital and thus, a comparison of the experimental data with simulated intensity distributions for different sample geometries allowed for a verification of the tilt angle with an accuracy of about 1°.

O 42.11 Tue 18:00 Poster D

Rubber-modified polybenzoxazine-based materials for surface coating applications — ●EUGENE B. CALDONA¹, AL CHRISTOPHER C. DE LEON², BRYAN B. PAJARITO³, and RIGOBERTO C. ADVINCULA² — ¹Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, USA — ²Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, USA — ³Department of Chemical Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines

This work demonstrates the preparation of rubber-modified polybenzoxazine (PBZ) where additives such as graphene oxide (GO), polyaniline (PANI), and nano-silica (SiO₂) are added separately and the resulting materials are used as surface coatings. PBZ is known for its near-zero shrinkage upon polymerization, chemical resistance, and good dielectric, thermal, and mechanical properties. PBZ has low surface free energy and low water absorption making it an excellent candidate for protective coating study. GO is added because of its ability to form a tortuous path leading to reduced permeability and enhanced barrier property. PANI, a conducting polymer, promotes passivation by forming a thin layer of metal oxides that further increase the anodic protection of the coating. Lastly, on top of providing superior corrosion protection, nano-SiO₂ introduces surface roughness that results in excellent anti-wettability, anti-icing, self-cleaning property, and superoleophilicity. Combined with good thermal and adhesion properties, the rubber-modified PBZ with different additives are said to be very promising surface coating materials for a variety of applications.

O 42.12 Tue 18:00 Poster D

Growth Inhibition of <i>P. Fluorescens</i> Biofilms by Ag/Teflon-Like Thin Films: A Comparative Morphological and Spectroscopic Study — ●MARIA CHIARA SPORTELLI¹, RUGGIERO QUARTO¹, ERHAN TÛTÛNCÛ², ANTONIO VALENTINI³, CHRISTINE KRANZ², and NICOLA CIOFFI¹ — ¹Chemistry Department, University of Bari, V. Orabona, 4-70126 Bari, Italy. — ²Institute of Analytical and Bioanalytical Chemistry, Ulm University, Albert Einstein Allee, 11 * 89081 Ulm, Germany — ³Dipartimento Interateneo di Fisica *M. Merlin*, University of Bari, V. Orabona, 4-70126 Bari, Italy

Ag-Teflon-like (Ag-CFx) composites were obtained by ion beam co-sputtering of polytetrafluoroethylene (PTFE) and Ag targets. AgNPs

are already used as antimicrobials in health industry, for food storage, in environmental applications. There is an increasing need of anti-biofouling surfaces and materials, to prevent biofilm formations. Biofilms, i.e. colonies of microorganisms embedded in an extracellular polymeric matrix, are a major cause of healthcare-associated infections, since bacteria are highly resistant to antimicrobials. In this perspective, the inhibition of biofilm growth is a crucial issue in the prevention of bacterial infections. In the present study, Ag-CFx composites were characterized by TEM, AFM, XPS and AAS. They were also deposited onto ZnSe ATR crystals. This approach allowed real-time monitoring of *P. fluorescens* biofilm growth and inhibition induced by the antimicrobial coating. These findings were corroborated by AFM imaging of bacteria incubated on Ag-CFx films.

O 42.13 Tue 18:00 Poster D

Electrospray Ion-Beam Deposition: UHV-deposition of non-volatile molecules — •SABINE ABB¹, HANNAH OCHNER¹, SVEN

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The standard technique to deposit molecules in ultra-high vacuum (UHV) is evaporation/sublimation. However, evaporation is limited to volatile molecules, e.g. molecules that can be brought in the gas phase without decomposition by heating. Electrospray Ion-Beam deposition gives access to non-volatile molecules of different classes, such as biomolecules, dyes and other complex molecules and therefore expands the range of samples in UHV. Employing the possibility of mass spectrometry and subsequent mass filtering, highly pure samples can be fabricated.

In this poster, we will show an overview of the recent work performed with our home-built electrospray ion-beam deposition instrument in conjunction with STM.