

O 40: Organic Molecules at Surfaces 4: Chemistry on Surfaces

Time: Wednesday 10:30–12:45

Location: S051

O 40.1 Wed 10:30 S051

On-surface synthesis of planar π -extended cycloparaphenylenes featuring an all-armchair edge topology — FEIFEI XIANG¹, SVEN MAISEL², SUMIT BENIWAL¹, VLADIMIR AKHMETOV^{2,3}, CORDULA RUPPENSTEIN³, MIRUNALINI DEVARAJULU¹, ANDREAS DÖRR¹, OLENA PAPAANINA³, ANDREAS GÖRLING², KONSTANTIN AMSHAROV^{2,3}, and SABINE MAIER¹ — ¹FAU Erlangen-Nürnberg, Dept. of Physik — ²FAU Erlangen-Nürnberg, Dept. of Chemistry and Pharmacy — ³Institute for Chemistry, University Halle-Wittenberg

[n]cycloparaphenylenes ([n]CPPs) have attracted significant attention due to their unique cyclic structure and highly effective para-conjugation leading to a myriad of fascinating (opto-)electronic properties. However, their strained topology prevents the π -extension of CPPs to convert them either into armchair nanobelts or planarized CPP macrocycles. We have successfully tackled this long-standing challenge and present the bottom-up synthesis and characterization of atomically precise in-plane π -extended [12]CPP on Au(111) by low-temperature scanning probe microscopy/spectroscopy combined with density functional theory.[1] The planar π -extended CPP represents the first nanographene with an all-armchair edge topology. The exclusive para-conjugation at the periphery yields delocalized electronic states and the planarization maximizes the overlap of p-orbitals, which both reduce the bandgap compared to conventional CPP. Calculations predict ring currents and global aromaticity in the doubly charged system.

[1] F. Xiang et al., Nat. Chem. 2022, doi: 10.1038/s41557-022-00968-3.

O 40.2 Wed 10:45 S051

Electronic Properties of N-Heterotriangulene based Charge Transfer Complexes — MOHSEN AJDARI¹, RONJA PAPPENBERGER¹, INA MICHALSKY², LEONIE PAP¹, CHRISTIAN HUCK¹, MARVIN HOFFMANN³, FRIEDRICH MAASS¹, MILAN KIVALA², ANDREAS DREUW³, and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Universität Heidelberg — ²Organisch-Chemisches Institut, Centre for Advanced Materials, Universität Heidelberg — ³Interdisziplinäres Zentrum für Wissenschaftliches Rechnen, Universität Heidelberg

N-heterotriangulenes (N-HTAs) are a class of organic electron-transporting semiconductors that belong to N-heteropolycyclic aromatic compounds, which are promising candidates for a variety of (opto) electronic applications. In this study, electronic high-resolution electron energy loss spectroscopy (HREELS) in combination with quantum-chemical theory are utilized to investigate the electronic properties of two N-HTA derivatives, N-HTA-550 and N-HTA-557 on Au(111). In addition, formation of charge transfer complexes (CTCs) with N-HTAs, acting as donor molecules in combination with two well-known cyano-based electron acceptor molecules, TCNQ and F4TCNQ is identified. Our findings indicate that formation of the 7-membered ring in N-HTA-557 by adding the -C=C- bridge leads to a narrowing of the optical gap size by 0.9 eV and a decrease in the first triplet state energy by 1.2 eV. Moreover, all donor/acceptor bilayer systems on Au(111) exhibit low-lying electronic transitions between 0.9 and 2.2 eV, which are attributed to the formation of CTCs.

O 40.3 Wed 11:00 S051

N-Heterotriangulenes Donors and Charge Transfer Complexes formed with strong Electron Acceptors investigated with Two-Photon Photoemission Spectroscopy — JAKOB STEIDEL¹, INA MICHALSKY², MILAN KIVALA², and PETRA TEGEDER¹ — ¹Institute of Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg — ²Institute of Organic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg

Many opto-electronic devices such as organic photovoltaic cells or organic light emitting diodes utilize donor-acceptor-systems (D-A-systems). Triphenylamine derivatives are promising candidates for donors in D-A-systems.1 The introduction of an etheno-bridge in the planar triphenylamine derivative indolo[3,2,1-jk]carbazole (N-HTA-550) creates a seven membered antiaromatic ring in the resulting N-Heterotriangulene-557 (N-HTA-557). While the molecular geometry is mostly preserved, the electronic structure is strongly modified by this additional -C=C-moiety.

In the present contribution we study the electronic properties of N-

HTA-550 and N-HTA-557 on a Au(111) surface using two-photon photoemission (2PPE) spectroscopy and temperature programmed desorption (TPD). Furthermore the formation of charge transfer complexes with strong electron acceptors (TCNQ and F4TCNQ) is investigated utilizing both 2PPE and TPD.

O 40.4 Wed 11:15 S051

Remarkably table metal-organic networks on an inert substrate: Ni-, Fe-, and Mn-TCNQ on graphene — ZDENĚK JAKUB¹, ANNA KUROWSKÁ¹, ONDREJ HERICH¹, LENKA ČERNÁ¹, LUKÁŠ KORMOS¹, AZIN SHAHSAVAR¹, PAVEL PROCHÁZKA¹, and JAN ČECHAL^{1,2} — ¹CEITEC, Brno University of Technology, Czechia — ²Faculty of Mechanical Engineering, Brno University of Technology, Czechia

Potential applications of 2D metal-organic frameworks (MOF) require the frameworks to be monophasic and well-defined at the atomic scale, to be decoupled from the supporting substrate, and to remain stable at the application conditions. Here, we present three systems meeting this elusive set of requirements: M-TCNQ (M = Ni, Fe, Mn) on epitaxial graphene/Ir(111). We study the systems experimentally by scanning tunneling microscopy, low energy electron microscopy and x-ray photoelectron spectroscopy. When synthesized on graphene, the 2D M-TCNQ MOFs are monophasic with M₁(TCNQ)₁ stoichiometry, and we demonstrate their remarkable chemical and thermal stability: All the studied systems survive exposure to ambient conditions, with Ni-TCNQ doing so without any significant changes to its atomic-scale structure or chemical state. Thermally, the most stable system is Fe-TCNQ which remains stable above 500 °C, while all the tested MOFs survive heating to 250 °C. Overall, the modular M-TCNQ/graphene system combines the atomic-scale definition required for fundamental studies with the robustness needed for applications, thus it presents an ideal model for research in single atom catalysis or spintronics.

O 40.5 Wed 11:30 S051

Control of overlayer-substrate coupling via alkali doping in two-dimensional metal-organic networks — BILLAL SOHAIL¹, PHIL J. BLOWEY², TIEN-LIN LEE³, PAUL T. P. RYAN³, DAVID A. DUNCAN³, GIOVANNI COSTANTINI¹, D. PHIL WOODRUFF¹, and REINHARD J. MAURER¹ — ¹University of Warwick — ²University of Leeds — ³Diamond Light Source

We characterise a two-dimensional donor-acceptor network formed by coadsorption of alkali atoms and the prototypical acceptor molecule TCNQ (7,7,8,8-tetracyanoquinodimethane) at different orientations of Ag surfaces. We characterise the adsorption structure with a combination of normal incidence x-ray standing wave (NIXSW) measurements, Scanning Tunneling Microscopy, and dispersion-inclusive Density Functional Theory, which we find to be in excellent agreement with experiment. The adsorption structure sensitively depends on an inter-play of molecule-metal charge transfer and long-range dispersion forces, which are influenced by the co-adsorption ratio between alkali atoms and TCNQ. In general, alkali atom co-adsorption reduces the molecule-substrate interaction strength, yet is energetically favoured compared to TCNQ co-adsorption with Ag adatoms. We show that the donor-acceptor ratio in the network is able to control the overlayer-substrate interaction, which strongly affects electronic properties such as the work function and the level alignment at the interface. Therefore, the concentration of alkali donor atoms can be used to tune electronic properties of the interface.

O 40.6 Wed 11:45 S051

Analysis of the 3-dimensional adsorption configuration of organic molecules by SPM manipulation and imaging — ALEXANDER IHLE¹, DANIEL EBELING¹, DANIEL KOHRS², HERMANN A. WEGNER², and ANDRE SCHIRMEISEN¹ — ¹Institute of Applied Physics, Justus Liebig University Giessen — ²Institute of Organic Chemistry, Justus Liebig University Giessen

On-surface chemistry is a powerful tool for building covalent molecular structures such as chains, networks, or graphene nanoribbons (GNRs). In particular, the catalytic properties of the metal substrate as well as the 2D confinement facilitate the synthesis of new structures that are not accessible via solution chemistry. The Ullmann type coupling is one of the most frequently applied on-surface reac-

tion for synthesizing C-C bonded structures. However, only limited information is available about the three dimensional adsorption conformation of the molecular educts and how this affects the reaction pathway. Here, we studied on-surface reactions of 9-X-10-(1,1':3',1''-terphenyl-5'-yl)anthracene (X= bromine, iodine) on Cu(111), Ag(111) and Au(111). Using low-temperature atomic force microscopy with CO-functionalized tips, we can identify the precise adsorption conformation of the pristine molecules as well as the intermediate and final products. In particular, the three dimensional conformation of the intermediates strongly inhibits the intermolecular coupling reaction between the educts on all surfaces. Instead, intramolecular bond formation is observed.

O 40.7 Wed 12:00 S051

STM growth studies of 5,14-ol-5,14-diborapentacyclo on low-index coinage metal surfaces — ●WUN-CHANG PAN¹, JING QI¹, CARINA MÜTZEL², PAULA WEBER¹, FRANK WÜRTHNER², and MATTHIAS BODE¹ — ¹Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institut für Organische Chemie & Center for Nanosystems Chemistry (CNC), Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

In recent studies [1, 2], heteroatoms-doped precursors have frequently been used to polymerize graphene nanoribbons with a large variety of structures or dopant heteroatoms. Using cryogenic scanning tunneling microscopy, we investigated the structure of self-assembled 5,14-ol-5,14-diborapentacyclo (CM218) on low-index coinage metal surfaces. The main focus of our study is on CM218 on Ag(111), where we find that molecular clusters and chains coexist with molecular islands. At low annealing temperature $T_{ann} < 100^\circ\text{C}$, the islands exhibit a rail track-like structure with a rhomboid-shaped unit cell. Besides, we find irregular clusters and molecular chains. At higher $T_{ann} \geq 180^\circ\text{C}$, islands with a honeycomb (HC) structure are observed. Topographic images of these HCs display a pronounced bias dependence. Molecule-functionalized tips allow for high-resolution images of these structures for which we suggest structural models.

[1] L. Grill and S. Hecht, *Nature Chemistry* 12, 115 (2020).

[2] Q. Zhong *et al.*, *Nature Chemistry* 13, 1133 (2021).

O 40.8 Wed 12:15 S051

Surface chemistry of dibromoindigo - effects of temperature and type of surface — ●MANUELA HOCKE^{1,2}, MICHAEL SCHMITTEL³, WOLFGANG HECKL^{1,2}, and MARKUS LACKINGER^{1,2} — ¹Deutsches Museum, 80538 München — ²Technische Universität München, Physics Department, 85748 Garching — ³Center of Micro and Nanochemistry, Universität Siegen, 57068 Siegen, Germany

Mother Nature offers a great variety of suitable halogenated compounds, which can readily be used as precursor for on-surface Ullmann couplings. Here, we study the thermally activated surface chemistry of the famous dye Tyrian purple (6,6'-dibromoindigo) comparatively on Ag(111) and Au(111) by Scanning-Tunneling-Microscopy. On Au(111) we observed two distinct self-assembled structures comprised of fully intact molecules. Covalent structures were obtained either by deposition onto hot surfaces or subsequent heating, where the heating rate is crucial. On Ag(111) only one self-assembled structure was observed. The organometallic structures obtained upon debromination rarely exhibited the anticipated linear structure. Instead, we find remarkably diverse structures. The additional functionalization of 6,6'-dibromoindigo with potent H-bond donor and acceptor groups renders the on-surface polymerization of this compound particularly prone to additional influences of supramolecular bonds with a vivid contribution of the co-adsorbed dissociated bromine atoms. Moreover, the surprisingly large variation of the organometallic structures on Ag(111) and the profound dependence on preparation parameters indicate an unexpectedly large kinetic influence.

O 40.9 Wed 12:30 S051

Interface-driven Assembly of Pentacene/MoS₂ Lateral Heterostructures: A Combined STM and DFT Study — ●SERGIO TOSONI¹, FRANCESCO TUMINO², ANDI RABIA², ANDREA LI BASSI², and CARLO CASARI² — ¹Dipartimento di Scienza dei materiali, Università di Milano-Bicocca, via Roberto Cozzi 55, I-20125 Milano, Italy — ²Dipartimento di Energia, Politecnico di Milano, via G. Ponzio 34/3, Milano, I-20133, Italy

Mixed-dimensional van der Waals heterostructures formed by molecular assemblies and 2D materials provide a novel platform for fundamental nanoscience and future nanoelectronics applications. Here we investigate a hybrid heterostructure between pentacene molecules and 2D MoS₂ nanocrystals deposited on Au(111) by means of Scanning Tunneling Microscopy and Density Functional Theory calculations.

In the MoS₂/Au interface, the lattice mismatch leads to the growth of extended monolayer films displaying a non-commensurate lattice with the metal substrate and typical features of point defects, identified as single sulfur vacancies.

The formation of atomically thin pentacene/MoS₂ lateral heterostructures is observed on the Au substrate. Interestingly, the inner regions of the MoS₂ layer are not covered by pentacene. The density of states changes sharply across the pentacene/MoS₂ interface indicating a weak interfacial coupling, which leaves unaltered the electronic signature of MoS₂ edge states. This work unveils the growth of abrupt lateral heterostructures toward hybrid devices based on organic/inorganic one-dimensional junctions.