O 6: Organic molecules on inorganic substrates: Adsorption and growth I

Time: Monday 10:30–12:30 Location: TRE/PHYS

O 6.1 Mon 10:30 TRE/PHYS

Support-dependent reactivity of Fe-DCA 2D Metal-Organic Frameworks — •Dominik Hrůza[1], Zdeněk Jakub[1], Jakub Planer[1], Tadeáš Lesovský[2], Ayesha Jabeen[1], Pavel Procházka[1], and Jan Čechal[1,2] — [1]CEITEC - Central European Institute of Technology, Brno University of Technology, Purkyňova 123, Brno 61200, Czechia — [2]Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896/2, Brno 61200, Czechia

2D Metal-Organic Frameworks (2D MOFs) are promising materials for applications in catalysis, sensing and spintronics. 2D MOFs based on 9,10-dicyanoanthracene (DCA) linker molecules are particularly intriguing due to their recently demonstrated magnetic and topological properties. Here, we study the reactivity of Fe-DCA supported on two weakly-interacting supports: graphene/Ir(111) and Au(111). Using Scanning Tunneling Microscopy (STM), X-Ray Photoemission Spectroscopy (XPS) and Low-Energy Electron Microscopy/Diffraction (LEEM/LEED), we test how the Fe-DCA reacts with carbon monoxide and molecular oxygen. When the Fe-DCA is supported on graphene, the CO adsorbs on the Fe-sites at temperatures below 200 K, while O2 exposure causes structural collapse of the 2D MOF at room temperature. In contrast, when the Fe-DCA is supported on Au(111), it appears inert to CO adsorption. Overall, our results show how the chemical reactivity of 2D MOFs depends on the supporting surface, providing critical insights for the potential integration of MOFs into functional devices.

O 6.2 Mon 10:45 TRE/PHYS

LT-STM investigation of azulene-based molecular architectures on metal surfaces — •Suchetana Sarkar[1,4], Natasha Khera[1], Kwan Ho Au-Yeung[1,5], Renxiang Liu[1,2,3], Ji Ma[1,2,3], Xinliang Feng[1,2,3], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Chair of Molecular Functional Materials and Faculty of Chemistry & Food Chemistry, TU Dresden, 01062 Dresden, Germany — [3]Max Planck Institute of Microstructure Physics, Weinberg 2, Halle, Germany — [4]Present address: Department of Chemistry, Philipps-Universität Marburg, 35032 Marburg, Germany — [5]Present address: Physikalisches Institut, Karlsruhe Institute of Technology, Karlsruhe, Germany

Azulene-based molecules offer a unique platform for probing on-surface self-assembly and electronic structure due to their non-benzenoid topology and intrinsic dipole. Presented here are the investigations of two related systems: a cyclopenta[cd]azulene trimer (CPAT) and a phenyl-functionalized analogue (CPAT-Ph), using low-temperature scanning tunneling microscopy and spectroscopy. CPAT forms well-ordered homochiral domains on Au(111), whereas CPAT-Ph exhibits weak adsorption and high mobility on Au(111) and shows no ordered phases on Cu(110). Spectroscopy reveals clear electronic differences between the molecules and substrate-induced shifts for CPAT-Ph. Finally, the results of thermally induced ring-closing reactions are also shown, discussing routes toward on-surface synthesis of non-benzenoid nanographenes.

O 6.3 Mon 11:00 TRE/PHYS

Surface study of heteromolecular layers for charge injection: deprotonated carboxylic acids mixed with pentacene — •Jakub Planer[1], Veronika Stará[1], Pavel Procházka[1], and Jan Čechal[1,2] — [1]Central European Institute of Technology, Brno University of Technology, Czech Republic — [2]Institute of Physical Engineering, Brno University of Technology, Czech Republic

Heteromolecular organic films represent promising candidates for efficient charge-injection layers in organic optoelectronic devices. Using surface-science experiments together with ab-initio modeling, we investigate the structural and electronic properties of intermixed layers composed of fully deprotonated carboxylic acids and pentacene (PEN) on Ag(100) and Ag(111) substrates. Our work demonstrates that these molecules form blends capable of modulating the electrode work function by up to 0.5 eV, depending on the mixing ratio, while remaining stable during subsequent organic-semiconductor deposition. These findings underline the potential of mixed carboxylate–PEN layers as practical, robust charge-injection modifiers and show that various carboxylic acids can be effectively used in such heteromolecular interfaces [1,2].

[1] Stará, Veronika, et al. *Tunable Energy-Level Alignment in Multilayers of Carboxylic Acids on Silver.* Physical Review Applied, **18**, (2022)

[2] Krajňák, T. et al. *Robust Dipolar Layers between Organic Semiconductors and Silver for Energy-Level Alignment.* ACS Appl. Mater. Interfaces, **16**, (2024)

O 6.4 Mon 11:15 TRE/PHYS

Orientational Order of Phenyl Rotors on Triangular Platforms on Ag and Au(111) — Richard Berndt[1], Richard Berndt[2], Richard Berndt[2], Richard Berndt[3], and •Richard Berndt[1] — [1]Institut für Experimentelle und Angewandte Physik, CAU Kiel, Germany — [2]Otto-Diels-Institut für Organische Chemie, CAU Kiel, Germany — [3]Centro de Física de Materiales, Donostia-San Sebastián, Spain

We investigated trioxatriangulenium functionalized with phenyl on Ag(111) and Au(111) using low-temperature scanning tunneling microscopy (STM). On Ag, the molecules form hexagonal arrays and the orientations of the phenyl moieties are resolved. Moreover, STM images suggest a dimerization of the molecules. Density functional theory calculations reproduce the experimental data. Van der Waals interaction is the dominant binding mechanism. The apparent dimerization results from an asymmetry of the phenyl wavefunction, which reflects intramolecular hydrogen bonding between the ligand and an oxygen atom of the triangulenium platform. Direct long-range interaction between phenyl moieties across molecules and the intramolecular H bonding are decisive for the orientations of the phenyl moieties. Similar experimental results were obtained on Au(111).

O 6.5 Mon 11:30 TRE/PHYS

Adsorption and Isomerization of Azobenzene Tetramers on Au(111) — •Natasha Khera[1], Ebru Cihan[1], Franz Plate[1], Soyoung Park[2], Ningwei Sun[2], Dmitry A. Ryndyk[1,2], Franziska Lissel[2,3], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Leibniz Institute of Polymer Research Dresden, Germany — [3]Institute for Applied Polymer Physics, TU Hamburg, 21073 Hamburg, Germany

This work investigates the manipulation and voltage-induced switching of star-shaped azobenzene tetramers [1] on Au(111) using low-temperature ultra-high vacuum scanning tunneling microscopy (LT-UHV STM) to study their adsorption behavior and cis-trans isomerization. On terraces, molecules in the trans state are highly mobile and difficult to image stably, whereas voltage induced switching to the cis state makes them immobile for reliable measurement. The study also utilizes step-edge sites where trans molecules are more stable and can be addressed without prior switching. Voltage pulses with the STM tip produces reproducible switching between high-contrast and low-contrast STM signatures, consistent with the cis-trans isomerization of the azobenzene core. Electric-field-dependent measurements are also performed by retracting the STM tip and recording tip-height vs bias characteristics, providing insight into the electric-field driven response of the molecules.

[1]. M. Baroncini, et al. Nature Chemistry 7, 634-640, (2015)

O 6.6 Mon 11:45 TRE/PHYS

Steering interfacial molecular self-assembly by substrate-molecule charge transfer — •Benjamin Achatz, Matthias Zeilerbauer, Marco Thaler, and Laerte Patera — Department of Physical Chemistry, University of Innsbruck, Innsbruck, 6020, Austria

Scanning probe microscopy studies of organic molecules on metal substrates have furthered our understanding of substrate-molecule charge transfer processes [1]. On surface self-assembly of the electron acceptor C_{60} is driven by an interplay of short-range attractive Van der Waals forces and long-range repulsive electrostatic interactions [2]. Here we report the formation of an intermixed phase composed of C_{60} and Zn(II)-5,10,15,20-tetrakis(4-aminophenyl)porphyrin (Zn-TAPP) molecules on Ag(111). An approach combining scanning tunneling spectroscopy (STS) and Kelvin probe force microscopy (KPFM) was used to investigate the degree of substrate-molecule charge transfer for C_{60} in close-packed islands and a row-like intermixed structure. Analysis of our tunneling and force spectroscopy measurements revealed that mitigation of the coulomb repulsion drives the formation of the intermixed phase and promotes additional charge transfer to the C_{60} molecules. These results demonstrate that controlling long-range Coulomb interactions can steer the formation of distinct self-assembled structures on metal substrates, offering insights for the design of new charge-optimized molecular nanostructures.

[1] R. Otero et al., Surf. Sci. Rep. 72, 105 (2017).
[2] M. Švec et al., Phys. Rev. B 86, 121407 (2012).

O 6.7 Mon 12:00 TRE/PHYS

Nanostructuring of organic radicals on cobalt surfaces — •Arkaprava Das and M. Benedetta Casu — Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen, Germany

Organic radicals are potential candidates for groundbreaking applications like energy storage, quantum computing, and spintronics. To investigate the nature of the adsorption of the radical derivative molecules on cobalt surfaces, we investigate their electronic structure and morphology. The electronic structure at the interface is investigated by using X-ray photoelectron spectroscopy (XPS), and the morphology is studied with scanning electron microscopy. The radical/Co interface interactions have resulted in different nanostructures crucial for device fabrication, whereas changes in line shape of core level spectra confer direct evidence of changed electronic properties at the interface. Considering ecological requirements, we also endeavour to minimize the materials consumption by making the Co substrate reusable, which is in line with the principles of closed-loop circular economy.

O 6.8 Mon 12:15 TRE/PHYS

Competition between dative bonds and aromatic gains — •Jonas Brandhoff[1], Richard Berger[2], Felix Otto[1], Maximilian Schaal[1], Lorenz Brill[1], Oliver T. Hofmann[2], Peter Puschnig[3], Torsten Fritz[1], and Roman Forker[1] — [1]Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany — [2]Institute of Solid State Physics, Technical University Graz, Petersgasse 16, 8010 Graz, Austria — [3]Institute of Physics, University of Graz, Universitätsplatz 5, 8010 Graz, Austria

Upon molecular adsorption on a surface, a variety of interactions can occur. Identifying which mechanisms dominate this complex quantum-mechanical landscape is crucial for understanding molecule – surface coupling. One key factor in many π-conjugated systems is aromaticity – a fundamental concept in chemistry describing the energetic stabilization that arises from particular π-electron arrangements. To investigate how aromaticity competes with other adsorption-driven interactions, we study 5,7,12,14-pentacenetetrone (P4O) on different metal surfaces as a model system. P4O is a prototypical molecule expected to undergo aromatic stabilization upon adsorption, where charge transfer from the substrate modifies the topology of the occupied π-system and leads to a more energetically favorable configuration. Using photoemission orbital tomography measurements combined with density functional theory calculations, we show how hybridization with the surface can outweigh a potential aromatic stabilization, *not* necessarily maximizing the latter. We reveal a mechanism in which the unoccupied π-system of the molecule forms dative bonds with the substrate.