O 13: Organic Molecules on Inorganic Substrates: Adsorption and Growth

Time: Monday 15:00–17:30 Location: H8

O 13.1 Mon 15:00 H8

Identical Fe-N4 Sites with Different Reactivity: Elucidating the Effect of Support Curvature — •Dominik Hrůza[1], Zdeněk Jakub[1], Jakub Planer[1], Azin Shahsavar[1], Jiří Pavelec[2], and Jan Čechal[1,3] — [1]CEITEC - Central European Institute of Technology, Brno University of Technology, Czech Republic — [2]Institute of Applied Physics, TU Wien, Vienna, Austria — [3]Faculty of Mechanical Engineering, Brno University of Technology, Czech Republic

Understanding the atomic-scale mechanisms of single-atom catalysts (SACs) is pivotal for advancing their design and application. Using a 2D metal-organic framework (MOF) featuring Fe-N4 sites on a graphene/Ir(111) support, we uncover how the curvature of an inert substrate can significantly influence adsorption properties. We show that a 0.4 Å corrugation induced by the inert graphene/Ir(111) moiré leads to pronounced variations in adsorption energy of TCNQ (tetracyanoquinodimethane) molecules adsorbed on the 2D MOF. Molecules adsorbed above the "valleys" of the graphene/Ir moiré exhibit binding energies significantly stronger than those above the "hills," resulting in a temperature stability difference of over 60 °C. Our findings based on STM and DFT highlight those small structural distortions in SAC structure can profoundly impact the adsorption properties.

O 13.2 Mon 15:15 H8

Small atoms – large influence: Structural evolution upon dehydrogenation — •Jonas Brandhoff[1], Alina Preibsch[1], Richard Berger[2], Felix Otto[1], Roman Forker[1], Oliver T. Hofmann[2], and Torsten Fritz[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

Molecular self-assembly is governed by the delicate balance between molecule-substrate and intermolecular interactions. Surface reactions can modulate this balance, enabling the engineering of tailored molecular architectures. Dehydrogenation is one of such surface reactions. Despite hydrogen being often overlooked as the smallest atom, its removal can significantly alter molecular interactions. In this study, 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) serves as a prototypical molecule to investigate dehydrogenation processes on surfaces. HHTP contains six equivalent hydroxy groups, allowing for varying degrees of dehydrogenation. These can be controlled via variation of the substrate temperature during deposition or using annealing steps post-deposition. Utilizing distortion-corrected Low-Energy Electron Diffraction (LEED), Scanning Tunneling Microscopy (STM), and Density Functional Theory (DFT), we examine the structural properties of (dehydrogenated) HHTP monolayers on Cu(111). Our analysis reveals distinct HHTP motifs and elucidates their interactions, providing deeper insights into the design of molecular architectures through controlled surface chemistry.

O 13.3 Mon 15:30 H8

Optical and Electronic Properties of Epitaxial Lead Phthalocyanine Monolayers and Bilayers on Graphite and Graphene — •Roman Forker, Marco Gruenewald, Matthias Spoddeck, and Torsten Fritz — Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Helmholtzweg 5, 07743 Jena, Germany

The optical and electronic properties of the near-infrared absorber lead phthalocyanine (PbPc) on graphitic surfaces are measured by means of differential reflectance spectroscopy (DRS) and scanning tunneling spectroscopy (STS), respectively. This is corroborated by a thorough structural characterization using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED), demonstrating the similarity of the adlayer structures on graphite and graphene substrates. The dielectric function of PbPc monolayers (ML) extracted from our DRS measurements exhibits monomer character, and thus provides evidence that there is no significant electronic coupling between the molecular film and graphite or graphene. From 1 to 2 ML the dielectric function changes drastically, indicating the formation of physical dimers. Concomitantly, for PbPc bilayers the electronic properties are found to be caused by the formation of face-to-face stacked molecules, resulting in a splitting of the dI/dV-features associated with the PbPc HOMO and LUMO upon bilayer formation. Our results are compared to previous photoelectron spectroscopy data of this system, where a similar splitting of the HOMO-related features was reported.

O 13.4 Mon 15:45 H8

Growth of N-heterocyclic carbenes on modified silicon surfaces — •Marie-Louise Fraser[1], Milan Kubicki[1], Ankita Das[2], Mowpriya Das[2], Preeti Chahar[2], Martin Franz[1], Frank Glorius[2], and Mario Dähne[1] — [1]Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Germany — [2]Universität Münster, Organisch-Chemisches Institut, Münster, Germany

Today's semiconductor industry is mainly based on silicon, thus the growth of organic films on silicon surfaces is a highly promising research field. However, the high number of dangling bonds typically present on silicon surfaces renders them often less suitable for molecular growth. With surface modifications more suitable silicon substrates can be produced. One such modification is a rare earth silicide layer on the Si(111) surface enabling growth of highly ordered monolayers [1]. Another suitable substrate is Si(111) modified by boron, as demonstrated e.g. for N-heterocyclic carbenes (NHCs) [2]. NHCs have been demonstrated to be particularly promising ligands for surface modification and functionalization. Here, scanning tunneling microscopy is used to examine the growth of the NHC molecule BIMe on both boron and rare-earth modified Si(111) surfaces. On both substrates, films with coverages ranging from submonolayers to complete monolayers could be successfully grown, allowing the determination of the adsorption geometry and of the ordering behavior in the monolayer. [1] M. Kubicki et al., *J. Phys. Chem. C* **128**, 13347 (2024). [2] M. Franz et al., *Nat. Chem.* **13**, 828 (2021).

O 13.5 Mon 16:00 H8

Imaging Dihydrogen Bond-Driven Assembly of Borazine on Au(111) — •Matthias Zeilerbauer, Marco Thaler, Barbara Obwaller, Milan Ončák, and Laerte L. Patera — Universität Innsbruck, Austria

Dihydrogen bonding (DHB) is a peculiar type of attractive interaction occurring between a partially positively charged hydrogen atom and a partially negatively charged hydrogen atom. Borazine represents a prototypical molecule exhibiting dihydrogen bonding in both gas phase, as well as in its crystalline form. For borazine assemblies on solid surfaces, a direct observation and characterization of dihydrogen bonding has remained elusive, possibly due to an intricate interplay of substrate-molecule and intermolecular interactions. Here we present evidence of dihydrogen bonding occurring in borazine assemblies on a Au(111) surface. By means of low-temperature scanning tunneling microscopy, we unveiled distinct configurations, exhibiting single and double dihydrogen bonding. Density functional theory calculations elucidate the interplay between substrate adsorption and intermolecular interactions to stabilize the formation of borazine dimers on Au(111), being the building blocks for the formation of larger assemblies.

O 13.6 Mon 16:15 H8

From Physical Trends to Structural Control: Insights into Phase Transition Times at Metal-Organic Interfaces — •Anna Werkovits, Simon B. Hollweger, and Oliver T. Hofmann — Institute of Solid State Physics, Graz University of Technology, Austria

At many metal-organic interfaces, molecules in the wetting layer undergo lying-standing transitions, significantly altering interface properties. Understanding the kinetics governing these transitions is essential for controlling structural evolution over time. This knowledge is particularly critical for tailoring interfaces based on either kinetically trapped or thermodynamically favoured structures.

To facilitate the design of interfaces, we develop a physically motivated surrogate model that estimates the phase transition times across a wide range of metal-organic interfaces. Using a systematic set of kinetic Monte Carlo simulations, incorporating variations in energetic landscapes and relative molecule sizes (representing hypothetical interface systems), we extract the physical relationships governing the timescales of phase transitions. These dependencies are analysed as functions of adsorption energies (lying and standing), kinetic barriers for reorientation and diffusion, molecule sizes, and environmental parameters such as temperature and pressure. This approach yields a formula that serves as a foundation for understanding trends, controlling structural evolution, and estimating timeframes for experiments and applications to ensure phase stability. Additionally, it enables the design of systems that remain stable over long periods, even in metastable states, advancing experimental and practical applications.

O 13.7 Mon 16:30 H8

Controlled Ion Beam Deposition supplied by Electrospray (ES-CIBD) - enabling UHV deposition of large, reactive or fragile building blocks for functional nano-architectures — •Andreas Walz[1,2], Annette Huettig[1,2], Michael Walz[1,2], Hartmut Schlichting[1,2], and Johannes V. Barth[2] — [1]pureions GmbH, Gilching, Germany — [2]Technical University of Munich, Germany

Cutting-edge research in the field surface- and nano- science using organic molecules requires control and unbiased understanding of structure and composition. Standard deposition techniques for the underlying building blocks restrict possible candidates: Thermal evaporation in vacuum (MBE, OMBE) is limited to volatile substances. Solution-based techniques such as drop casting, spin coating or inkjet printing are versatile but often lack purity and quality. Electrospray ionization (ESI) combined with mass selection and soft-landing of molecules unravels the vast potential of large, reactive or bio-relevant building blocks. The pool of possible molecules spans a wide spectrum from small organic molecules, over graphene nanoribbons (GNRs) up to several kilo- and megadalton proteins, DNA, but also inorganic clusters and larger nanoparticles may be possible. In-line with this, we present an UHV ion beam deposition device and its functionalities. Deposited layers are analyzed via STM. The main body of the device contains RF-driven ion guides with high transmission (>80% efficiency). A digital square-wave quadrupole mass filter (dQMF) provides virtually unlimited m/z-range. The footprint is benchtop in size, 0,5 x 1 m.

O 13.8 Mon 16:45 H8

Reactions of benzoporphyrins with Cu(111) — •Maximilian Muth, Majid Shaker, Julien Steffen, Alexander Wolfram, Simon Steinbach, Andreas Görling, Hans-Peter Steinrück, and Ole Lytken — Friedrich-Alexande-Universität Erlangen-Nürnberg, Germany

Porphyrins are molecules with many interesting properties that change upon adsorption on solid substrates. This can lead to something as simple as a change in conformation of the molecule or something more drastic as a reaction with - or catalyzed by - the substrate. We have focused on three molecules: free-base tetraphenyl transdibenzoporpyhrin, copper tetraphenyl transdibenzoporpyhrin and free-base tetraphenyl tetrabenzoporpyhrin adsorbed on Cu(111). Using temperature-programmed desorption, X-ray photoelectron spectroscopy, scanning tunneling microscopy and density-functional theory calculations, we have identified three reactions in the temperature range from 280 to 1000 K. In the first reaction step at 350 - 480 K the free-base benzoporphyrins react with copper atoms from the substrate, forming metalloporphyrins. At 480 - 650 K, the phenyl rings and pyrrole/benzo rings undergo a ring fusion reaction. Finally, at 650 - 950 K, the molecules polymerize and all remaining hydrogen atoms desorb from the surface as H2.

O 13.9 Mon 17:00 H8

Supercharging Polymorphism of Organic/Inorganic Interfaces — •Christoph Wachter and Oliver T. Hofmann — Institute of Solid State Physics, Graz University of Technology, Graz, 8010, Austria

The polymorphism of organic/inorganic interfaces heavily influences a multitude of their properties. Therefore, altering the polymorphism by changing the substrate or modifying the intermolecular interactions has been studied extensively. However, the extent to which charge transfer affects polymorphism has yet to be investigated systematically. Based on the hypothesis that there is a link between the band width of polymorphs and their relative energy, we expect that polymorphs with larger band width are preferred if charge is transferred uniformly across the organic monolayer.

Conversely, it is also possible for charge to localize in individual adsorbates instead of spreading out across the monolayer. Such localized charge transfer occurs when the electronic coupling of the organic molecules to each other and to the substrate is small. In that case the relation stated above is not well-defined anymore.

To investigate the impact of both localized and delocalized charge transfer on polymorphism, we employ density functional theory in conjunction with a machine-learning based structure search algorithm. To properly capture charge localization, we go beyond the standard semilocal functionals by utilizing hybrid functionals and report whether the expected relation still holds in the case of localized charge transfer.

O 13.10 Mon 17:15 H8

Towards 2D metal-organic frameworks on weakly interacting substrates: FeDCA on coinage metals and Bi_2Se_3(111) surfaces — •Anna Kurowská[1], Matthias Blatnik[1], Veronika Stará[1], Pavel Procházka[1], Čestmír Drašar[2], and Jan Čechal[1,3] — [1]Central European Institute of Technology, Brno University of Technology — [2]Faculty of Chemical technology, University of Pardubice — [3]Institute of Physical Engineering, Brno University of Technology, Czech Republic

The formation of 2D metal-organic frameworks (MOFs) on a surface of topological insulator (TI) is a promising path to design quantum materials with exotic properties. MOFs featuring ferromagnetically coupled metal atoms are theoretically predicted to induce an exchange gap in the TI's surface band structure, potentially leading to a quantum anomalous Hall effect. However, the knowledge of self-assembly on TI substrates is still scarce. Here, we demonstrate the first experimental realization of 2D MOF, Fe-dicyanoanthracene (FeDCA), on the surface of a strong TI Bi2Se3. The structure and morphology were studied via scanning tunneling microscopy (STM) and low-energy electron microscopy (LEEM) and diffraction (LEED). We compare the growth of FeDCA on the Bi_2Se_3(111) surface with coinage metals and gr/Ir(111) surfaces, and discuss the conditions at which we obtain typical mixed Kagomé-honeycomb lattice and at which a new hexagonal lattice appears. The demonstration of 2D MOF/TI hybrid material presents a milestone on the way toward their application in fault-tolerant spin interconnects in future quantum devices.