O 25: Organic Molecules on Inorganic Substrates III: Adsorption & Growth

Time: Tuesday 10:30–13:00 Location: MA 043

O 25.1 Tue 10:30 MA 043

(Meta)stable monolayers on metals: Kinetic trapping of the flat-lying phase — •Anna Werkovits[1], Simon B. Hollweger[1], Max Niederreiter[2], Thomas Risse[3], Johannes J. Cartus[1], Martin Sterrer[2], Sebastian Matera[4], and Oliver T. Hofmann[1] — [1]Institute of Solid State Physics, TU Graz — [2]Institute of Physics, KFU Graz — [3]Institut für Chemie und Biochemie, Freie Universität Berlin — [4]Theory Department, Fritz Haber Institute of the MPG

While conventional wisdom dictates that conjugated organic molecules on metals adopt a flat-lying configuration, recent studies indicate coverage-dependent shifts to upright-standing phases, which exhibit distinctly different physical characteristics. Our investigation challenges the prevailing notion by arguing that, from an energetic standpoint, thermodynamically stable upright-standing phases may be more widespread than previously believed. However, these phases are often not found experimentally due to kinetically trapping under typical experimental conditions. Using a combination of first principles kinetic Monte Carlo simulations and experiment, we show that during the growth process of organic molecules, phases with a lower molecular density (i.e., flat-lying molecules) are formed before the thermodynamically more stable upright standing phase. Notably, the transition to the upright-standing phases is frequently hindered kinetically in standard surface science conditions. Our exploration of growth conditions and interface energetics reveals that the phase transition time is primarily dictated by the deposition rate, and largely independent of the nature of the organic molecule.

O 25.2 Tue 10:45 MA 043

CoPc/F_{16}CuPc on Ag(100): Triggering the condensation of a 2D molecular gas — •Thorsten Wagner[1], Blazej Golyszny[2], Grazyna Antczak[2], and Peter Zeppenfeld[1] — [1]Institute of Experimental Physics, Johannes Kepler University Linz, Austria — [2]Institute of Experimental Physics, University of Wroclaw, Poland

When metal phthalocyanine molecules are deposited on metallic surfaces, they often form a 2D molecular gas in the submonolayer regime: Instead of a fixed position as in a condensed phase such as 2D islands, they are very mobile on the surface and change frequently their adsorption sites and geometry. The reason for this is a so-called surface-mediated repulsion, which may stabilizes the 2D gas phase even far beyond a coverage of 0.5 ML. This repulsion can be compensated by using mixtures of hydrogen- and fluorine-termined phthalocyanines. Here, we use photoelectron emission microsopy (PEEM) to investigate ultrathin films of cobalt-Pc (CoPc) and perfluorinated copper-Pc (F_{16}CuPc) on Ag(100) surfaces. By following the evolution of the standard deviation[1] of the image sequences acquired during subsequent deposition of the molecules, the 2D molecular gas and the condensed bi-molecular phase can be identified. Regardless of the sequence of deposition, first CoPc and then F_{16}CuPc or vice versa, we can trigger the condensation of the 2D gas into a dense structure with a 1:1 ratio of the two molecules. The mixing of the molecules is actually not limited to the first layer on the substrate.

[1] Th. Wagner et al. in Ultramicroscopy 233, 113427 (2022)

O 25.3 Tue 11:00 MA 043

Constructing chiral overlayers: From single molecules to closed layers — •Jonas Brandhoff[1], Fumi Nishino[2,3], Keisuke Fukutani[2,3], Marco Gruenewald[1], Maximilian Schaal[1], Felix Otto[1], Roman Forker[1], Satoshi Kera[2,3], and Torsten Fritz[1] — [1]Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany — [2]Institute for Molecular Science, Myodaiji, 444-8585, Okazaki, Japan — [3]The Graduate University of Advanced Studies, Hayama-cho, 240-193 Kanagawa, Japan

Recently, the interest in chiral molecules has spiked. The chirality-induced spin selectivity (CISS) promises a high spin-polarizability for electrons traversing a chiral molecule. However, the CISS effect is yet not fully understood. To be able to probe the CISS effect with area averaging methods like photoelectron spectroscopy a well-defined chiral surface, consisting of chiral molecules, is needed. In this study the chiral molecule BINAP is investigated on a Au(111) surface. To understand how chirality from one single molecule evolves into a fully chiral overlayer, a coverage dependent study, showing many different structural motifs of BINAP, was done. This structural evolution was investigated using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). In combination, these methods reveal a chiral lattice and the role of the different molecule-molecule and molecule-substrate interactions will be discussed. This study offers a deeper insight in the engineering of chiral surfaces and opens a possible pathway towards spintronic applications.

O 25.4 Tue 11:15 MA 043

Vibrational and structural analysis of P2O and P4O monolayers on Ag(111) and Ag(110) — •Ravi Priya, Keda Jin, Weishan Wu, and Peter Jakob — Department of Physics, Philipps-Universität Marburg, Germany

Various phases and associated phase transformations have been studied for 6,13-pentacenequinone (P2O) and 5,7,12,14-pentacenetetrone (P4O) on Ag(111) and Ag(110) using SPA-LEED, FTIRAS & TDS. For P2O, sub-monolayer regime is governed by formation of long rows, aligned along the [110] direction with varying distances between rows. The interaction along the rows is attractive and either weak or slightly repulsive between rows. Close to completion of the monolayer, the streaky LEED patterns turn into sharp, well-defined reflexes. For P4O, attractive intermolecular and molecule-metal interactions lead to ordered and uniform structures for sub-monolayers on both substrates. Lateral ordering is governed by orientation-dependent intermolecular interactions including steric hindrance and hydrogen bonding leading to distinct coverage and temperature-dependent phases on both substrates. IRAS suggests more prominent Interfacial Dynamical Charge Transfer (IDCT) for P4O vs P2O on Ag(111) due to a notably higher DOS of the P4O-LUMO at ε_F. Molecule-metal interaction is enhanced on Ag(110) vs Ag(111) for both molecules. Intensity, asymmetry, and line shape changes of IDCT-bands reflect the dynamics of vibrational modes and are associated with the DOS of the molecule-LUMO at ε_F along with the overall strength of respective molecule-metal interaction.

O 25.5 Tue 11:30 MA 043

Impact of alkyl side groups on the structure formation of merocyanines on the Ag(100) surface studied by STM, SPA-LEED, and NIXSW — •Anna Juliana Kny[1], Anja Haags[1], Sergey Subach[2], and Moritz Sokolowski[1] — [1]Clausius Institut für Physikalische und Theoretische Chemie, Universität Bonn, Germany — [2]Forschungszentrum Jülich, Germany

The control over the molecular packing is an important key aspect for the properties of molecular optoelectronic devices. In our study, we focus on the self-organization of merocyanine (MC) molecules which are in focus for applications due to high transition dipole moments.[1] Starting from the prototype MC 2-[5-(5-dibutylamino-thiophen-2-yl-methylene)-4-*tert*-butyl-5*H*-thiazol-2-ylidene]-malononitrile (HB238) [2] we systematically altered the length of the alkyl side groups and investigated their influence on the adsorption and ordering on the Ag(100) surface. We used SPA-LEED, STM, XPS, and NIXSW. Remarkably, a formation of homochiral tetrameric aggregates is observed for all investigated MCs, independently from their alkyl side groups. However, the side groups have a large impact on the lateral packing of the aggregates and the registry to the underlying Ag(100) surface. We present NIXSW data which give an additional insight to the surface bonding of the tetrameric aggregates. The MC were kindly provided by the Meerholz group (Cologne). We acknowledge experimental support from D. Duncan (DLS). Supported by the DFG through the research training group 2591 and the Diamond Light Source, UK. [1] JACS 137 (2015) 13524. [2] Nanoscale 15 (2023) 10319.

O 25.6 Tue 11:45 MA 043

Adsorption and Orientation of N-heterocyclic Carbenes and Olefines on Metallic Surfaces — •Felix Landwehr[1], Mowpriya Das[2], Sergio Tosoni[3], Juan Navarro[1], Ankita Das[2], Maximilian Koy[2], Markus Heyde[1], Gianfranco Pacchioni[3], Frank Glorius[2], and Beatriz Roldan Cuenya[1] — [1]Fritz-Haber Institute of the MPG, Berlin, Germany — [2]Westfälische Wilhelms-Universität, Münster, Germany — [3]Università di Milano-Bicocca, Milano, Italy

N-Heterocyclic carbenes (NHCs) have attracted scientific interest in recent years due to their excellent properties as surface modifiers with applications in materials science and catalysis. Structurally similar to

NHCs are N-heterocyclic olefins (NHOs), comprising of an additional terminal alkylidene moiety (CH2) at the carbene position. NHOs possess highly polarizable and remarkably electron-rich double bonds and have been effectively utilized as exceptional anchors for surface modifications. We investigated the adsorption, orientation and electronic properties of the sterically low-demanding IMe-NHO compared to its analogous IMe-NHC counterpart on a Cu(111) surface. High-resolution electron energy-loss spectroscopy (HREELS) measurements show a flat-lying ring adsorption configuration for both molecules. While the NHC adopts a dimer configuration including a Cu adatom, the NHO chemisorbs over a C-Cu bond perpendicular to the surface. This distinct difference leads for the NHOs to a higher net electron transfer from the surface compared to the NHCs. These results highlight the role of NHOs in surface science as they extend the functionalization capabilities of NHCs into stronger electronic modification.

O 25.7 Tue 12:00 MA 043

Passivation of a metal surface strengthens the binding of an N-heterocyclic carbene to a metalloporphyrin pedestal

— •Dennis Meier[1], Peter Knecht[1], Peter Feulner[1], Francesco Allegretti[1], Joachim Reichert[1], Johannes V. Barth[1], and Anthoula C. Papageorgiou[1,2] — [1]Technical University of Munich, Germany — [2]National and Kapodistrian University of Athens, Greece

The extension of well-ordered 2D self-assemblies to more complex 3D architectures in ultra-high vacuum will bridge the gap between atomically precise supramolecules and extended materials. It is therefore crucial to understand the binding of out-of-plane linker molecules. We recently introduced a strategy to use Ru-porphyrins as pedestals of N heterocyclic carbenes (NHCs) on a metal surface. Here, we present engineering of the Ru-porphyrin metal interface for a significant improvement in the thermal stability of such pedestal systems. The enhanced binding strength is achieved by introducing a layer of O atoms between the Ru porphyrins and the metal surface. We characterize unambiguously the chemical state, structure and thermal stability of NHC molecules adsorbed to Ru octaethyl porphyrin on Cu(110) and Cu(110)-(2x1)O by means of photoelectron spectroscopy, scanning tunneling microscopy and temperature programmed desorption. On Cu(110)-(2x1)O, more extended 2D domains of pedestals and an increment of NHC binding stability by around 130 K was realized.

O 25.8 Tue 12:15 MA 043

Molecular self-assembly of C_{60} on $CsPbBr_3(100)$

— •Hannah Loh, Andreas Raabgrund, and M. Alexander Schneider — Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

$CsPbBr_3$ is a promising alternative to organic-inorganic perovskites in solar cells. Aiming at higher efficiencies, the band alignment of the perovskites and the transport layers within the solar cell are a crucial parameter [1]. Evaporating the single components CsBr and $PbBr_2$ in a 1:1 stoichiometry, thin $CsPbBr_3$ films grow epitaxially in a (2×2) cell with respect to Au(100). For coverages greater than 5 ML two surface reconstructions, (2×2) and $\left(2\sqrt{2}\times\sqrt{2}\right)\mathrm{R}45^\circ$, of the $CsPbBr_3(100)$ are found [2].

In this contribution we exploit these films to investigate the self assembly of C_{60}, which is a known electron transport material in solar cells, on $CsPbBr_3$/Au(100) by STM, LEED and DFT. For submonolayer coverage of C_{60} we find hexagonal closed-packed islands with different alignments with respect to the substrate that are not influenced by the reconstruction. The C_{60} molecules within the islands show rotational orientation without apparent lateral order. After annealing to 420 K the islands become multilayer structures. STS measurements reveal a bandgap of 2.8 ± 0.1 eV for $CsPbBr_3$ and molecular states at 0.9 ± 0.1 eV (LUMO) and at 2.3 ± 0.1 eV (LUMO+1) in the monolayer C_{60} configuration.

[1] Schmidt-Mende et al., APL Materials, **9**, 109202 (2021)
[2] Rieger J. et al., Phys. Rev. Mat, **7**, 035403 (2023)

O 25.9 Tue 12:30 MA 043

Molecular adsorption on multidomain h-BN/Pt(111): Exploring 2D material behavior for different rotational domains

— •Rocío Molina-Motos[1] and Antonio J. Martínez-Galera[1,2,3] — [1]Departamento de Física de Materiales, Universidad Autónoma de Madrid, E-28049 Madrid, Spain. — [2]Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain — [3]Instituto de Ciencia de Materiales Nicolás Cabrera, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

Exploration into the domain of molecular adsorption on two-dimensional (2D) materials carries significant expectations, offering insights into unprecedented physicochemical phenomena and paving the way for the future development of nanodevices [1,2]. The present work explores the intricacies of the adsorption of the prototypic molecule Perylenetetracarboxylic dianhydride (PTCDA) on single layers of polycrystalline hexagonal boron nitride (h-BN) grown on Pt(111) surfaces, focusing on the structural and electronic properties of adsorbed molecules near domain boundaries. This research has been conducted under ultrahigh vacuum conditions, utilizing a variable temperature scanning tunneling microscope as the main characterization tool.

References:

[1] A. Kumar, K. Banerjee and P. Liljeroth. Nanotechnology 28, 082001 (2017).

[2] H. Guo, M. D. Jiménez-Sánchez, A. J. Martínez-Galera, J. M. Gómez-Rodríguez. Nanoscale 15, 5083-5091 (2023).

O 25.10 Tue 12:45 MA 043

Analysis of thiahelicene non-covalent molecular wires using nc-AFM

— •Gema Navarro[1], Antoine Hinaut[1], Shuyu Huang[1], Yunbin Hu[2], Thilo Glatzel[1], Akimitsu Narita[2], and Ernst Meyer[1] — [1]Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland. — [2]Max Plank Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany.

Helicene derivatives are widely used in the field of Circularly Polarized Organic Light-Emitting Diodes (CP-OLEDs)[1] due to their chiroptical properties. According to previous reports an enhancement in their optical response have been obtained by means of the self-assembled formation. The surface science studies are beneficial for the further comprehension of this phenomena. On surface, the zigzag twin row configuration constitutes by far the predominant molecular phase formed on metal surfaces, however factors such as temperature, surface nature and heteroatoms incorporation have been shown to have an strong influence in the self assembled pattern.

In this work, we addressed the study of the adsorption of a sulfur-containing double helicene on Cu(111) surface. Formation of non-covalent molecular wires, widely spread on the terraces, were observed after the deposit and gentle annealing. The wires symmetry indicates an strong influence with the surface. Furthermore, this configuration was observed at low, medium and high coverage regimen. All the images presented were acquired at room temperature by means a home-built nc-AFM microscope under UHV conditions.

[1] Meng, G. et al. Adv. Mater. 2023, 2307420.