O 47: Poster Session IV: Organic molecules on inorganic substrates: networks and overlayers

Time: Tuesday 13:30–15:30 Location: P

O 47.1 Tue 13:30 P

Alkali Doping Leads to Charge-Transfer Salt Formation in a Two-Dimensional Metal Organic Framework — •Billal Sohail[1], Phil Blowey[1,3], Giovanni Costantini[1], Phil Woodruff[2], and Reinhard J. Maurer[1] — [1]Department of Chemistry, University of Warwick, UK — [2]Department of Physics, University of Warwick, UK — [3]Department of Chemistry, University of Leeds, UK

A detailed characterisation of structure and electronic properties at metal-organic interfaces is crucial for the design of novel molecular electronic devices such as organic photovoltaics (OPVs). In such devices, strong donors such as alkali atoms and acceptor molecules, such as TCNQ (7,7,8,8,-tetracyanoquinodimethane), are added to organic electronics devices to tune the charge interjection properties at the metal-organic interfaces. We present a joint computational and experimental study to examine the intricate coupling of geometry and electronic structure of TCNQ coadsorbed with potassium atoms on Ag(111), which forms a strongly interacting organic salt. Conversely, pure TCNQ on Ag(111) forms strongly surface-bound adlayers containing silver adatoms. Quantitative agreement between theory and experiment required the rescaling of dispersion coefficients to account for strong charge transfer. We further identify the energetic driving force for organic salt formation and discuss the intricate competition between donor, acceptor and metal substrate.

O 47.2 Tue 13:30 P

Metalation of 2HTCNPP on Ag(111) with Zn - evidence for the sitting atop complex at room temperature — •Jan Kuliga[1], Rodrigo Cezar de Campos Ferreira[2], Rajan Adhikari[1], Stephen Massicot[1], Michael Lepper[1], Helen Hölzel[3], Norbert Jux[3], Hubertus Marbach[1], Abner de Siervo[2], and Hans-Peter Steinrück[1] — [1]Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — [2]Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Campinas, 13083-859, SP, Brazil — [3]Organische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nikolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany

Using STM at RT, we study the adsorption of the free base 2HTCNPP on Ag(111), and its metalation to ZnTCNPP by post-deposition of Zn atoms. The goal is to obtain further insights in the metalation reaction and the influence of the cyanogroups on this reaction. The interaction of 2HTCNPP with post-deposited Zn leads to the formation of three different 2D ordered island types that coexist on the surface. All contain a new species with a bright appearance, which increases with the amount of post-deposited Zn. We attribute this to metastable SAT (*sitting atop*) complexes formed by Zn and the macrocycle, that is, an intermediate in the metalation reaction to ZnTCNPP, which occurs upon heating to 500 K. Interestingly, the activation barrier for the successive reaction of the SAT complex to the metalated ZnTCNPP species can also be overcome by a voltage pulse applied to the STM tip.

O 47.3 Tue 13:30 P

Self-assembled 2D-coordination-Kagome, quadratic and closed-packed-hexagonal lattices formed from cyano-functionalized benzo-porphyrins on Cu(111) — •Rajan Adhikari[1], Jan Kuliga[1], Michael Ruppel[2], Norbert Jux[2], Hubertus Marbach[1], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — [2]Lehrstuhl für Organische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nikolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany

We investigated the adsorption of 2H-TCNPTBP molecules on the Cu(111) surface by scanning tunneling microscopy in UHV at RT. Three types of network structures are observed to coexist at low coverages. The first two Kagome lattice and the quadratic pattern are stabilized by cyano-Cu-cyano interactions with Cu adatoms; the other is a close-packed hexagonal network, which is stabilized by H-bonds and dipole-dipole interactions of oppositely oriented cyano-end groups. The hexagonal network has a molecular density on the surface, which is a factor of 2.3 larger than that of the Kagome lattice and the quadratic structure, which is attributed to the energy gain upon adsorbing a higher number of molecules. This finding leads us to suggest a coverage dependent competition between strong metal-organic coordination bonds at low coverage and weak hydrogen bonds plus dipole-dipole interactions at high coverage. The results show that a subtle interplay between adsorbate-substrate and adsorbate-adsorbate interactions can steer on-surface metal-organic coordination.

O 47.4 Tue 13:30 P

Functional 1D template to drive the assembly and alignment of polycyclic molecules — Valeria Chesnyak[1,2], •Marc G Cuxart[1], Knud Seufert[1], and Willi Auwärter[1] — [1]Physics Department E20, Technical University of Munich, Garching, Germany — [2]IOM-CNR Laboratorio TASC, Trieste, Italy

Two-dimensional (2D) materials grown on metal substrates constitute excellent platforms to engineer the properties of organic molecules and molecular arrays [1,2]. Moiré superstructures emerging from the combination of distinct symmetries and periodicities of metal surface and 2D layer can guide the self-assembly of molecules, while the nature of the 2D layers and their interfacial properties determine the electronic (de)coupling between molecules and metal.

Here we present the formation of a one-dimensional (1D) template resulting from the growth of a 3-fold symmetric hexagonal boron nitride (*h*BN) layer on a 4-fold symmetric Ir(100) surface. Its functionality is probed by subsequent deposition of pentacene molecules and comprehensive characterization by STM, STS, LEED and XPS measurements. This reveals a linear alignment of individual molecules, shows that the templating functionality originates due to a 1D modulation of the work function, and indicates an electronic decoupling of the molecules from the metal. This system represents a suitable 1D template that provides prospect for the study of arrays of aligned molecules and other low-dimensional nanostructures.

[1] W. Auwärter, Surf. Sci. Rep. 74(1) (2019)
[2] A. Kumar *et al.*, Nanotechnology 28(8) (2017)

O 47.5 Tue 13:30 P

On-surface assembly of supramolecular graphyne-like 2D materials: from hydrogen- and halogen-bonded to organometallic networks — Zechao Yang[1], Lukas Fromm[2], Tim Sander[1], Julian Gebhardt[2], Tobias Schaub[3], Himadri Soni[2], Binbin Da[1], Andreas Görling[2], Milan Kivala[3], and •Sabine Maier[1] — [1]Department of Physics, FAU Erlangen-Nürnberg — [2]Chair of Theoretical Chemistry, FAU Erlangen-Nürnberg — [3]Organisch-Chemisches Institut, Universität Heidelberg

The on-surface assembly of graphyne-based 2D materials are directive for the synthesis of the elusive carbon allotrope graphyne. Here, we demonstrate a supramolecular approach to fabricate highly-ordered monolayered hydrogen- and halogen-bonded [1] as well as organometallic graphyne-like 2D materials [2] from functionalized triethynyltriazine derivatives on Au(111) and Ag(111). The supramolecular graphynes have been investigated by STM in combination with DFT. We found that the halogen-bondend networks with N. . . Br-C(*sp*)-bonds lead to significantly stronger bonded networks compared to the hydrogen-bonded networks with N. . . H-C(*sp*)-bonds. For the organometallic networks with Ag-bis-acetylide bonds, large-area networks of several hundred nanometers with topological defects at domain boundaries are obtained. The thermodynamically controlled growth mechanism is explained through the direct observation of intermediates, which differ on Ag(111) and Au(111).

[1] Z. Yang et al. Angew. Chem. Int. Ed., 59, 24, 9549-9555 (2020)
[2] Z. Yang et al. ACS Nano, 14, 12, 16887-16896 (2020)