O 65: Poster: Molecular Nanostructures on Surfaces

Time: Wednesday 18:00–20:00 Location: Poster C

O 65.1 Wed 18:00 Poster C

On surface synthesis of a Dicaesium Tetraphenylporphyrin Complex: A combined TPR, XPS, STM and DFT study — •Kassandra Zoltner, Leonard Neuhaus, Florian Münster, Lukas Heuplick, Jan Herritsch, and J. Michael Gottfried — Department of Chemistry, University of Marburg, 35043 Marburg, Germany

Tetrapyrroles such as porphyrins and their metal complexes exhibit interesting chemical and optoelectronic properties leading to numerous potential applications in photosensor technology and organic electronics. While the surface chemistry of transition metal-porphyrin complexes has been extensively studied, there is a growing interest in exploring complexes with alkali metals. This study focuses on the on-surface reaction of tetraphenylporphyrin (H_2TPP) with caesium in the multilayer and monolayer regime on Ag(111). The reaction product was conclusively identified by temperature programed desorption mass spectrometry (TPD-MS) as Cs_2TPP, where both aminic hydrogens were replaced by caesium ions. The data also indicate that Cs_2TPP is thermally stable up to 700 K. Upon annealing up to 400 K the N1s X-ray photoelectron spectrum revealed a complete metalation to Cs_2TPP in the monolayer, whereas in the multilayer a partial conversion is already observed at room temperature. DFT calculations indicate that Cs_2TPP exhibits a bipyramidal structure with Cs ions on both sides of the molecular plane. The conducted study sheds light on the on-surface coordination chemistry of heavy alkali metal tetrapyrrole complexes potentially leading to further improvement and advancements in modern technologies.

O 65.2 Wed 18:00 Poster C

Step reconstruction from metal-molecule interaction — •Julie Teerink, Aleš Cahlík, Danyang Liu, Carolina A. Marques, and Fabian D. Natterer — Department of Physics, University of Zurich, Winterthurerstrasse 190, CH-8057, Switzerland

The model system for metal-molecule interaction PTCDA/Ag(111) shows diverse structural phases and strong charge-transfer. Co-adsorption of PTCDA and Ag-adatoms leads to substantial mass transfer and restructuring of the substrate surface. The PTCDA molecules embed themselves into Ag step edges, which strongly curve and form isolated Ag step-spirals or Ag islands, depending on the presence of substrate screw dislocations. These islands and step-spirals show 2D and 1D quantum confinement of the Ag surface state. To investigate the relationship between molecule length and step curvature, we co-deposit Ag-adatoms with NTCDA, a molecule with the same oxygen-carbon bonds as PTCDA but with a smaller carbon backbone.

O 65.3 Wed 18:00 Poster C

Synthesis and Characterization of Pentadecacene by Tip-manipulation with a Scanning Probe Microscope — •Grigori Pasko[1], Zilin Ruan[1], Tim Naumann[1], Jakob Schramm[2], John Bauer[3], Holger F. Bettinger[3], Ralf Tonner-Zech[2], and J. Michael Gottfried[1] — [1]University of Marburg, 35043 Marburg, Germany — [2]University of Leipzig, 04103 Leipzig, Germany — [3]University of Tübingen, 72076 Tübingen, Germany

Carbon nanomaterials exhibit versatile electronic properties that potentially can be exploited in the field of organic semiconductors. The acene series is an interesting class of compounds consisting of linearly fused polycyclic aromatic hydrocarbons (PAHs). The description as a closed-shell system becomes inadequate for long acenes as their (poly-)radical character increases. The resulting enhanced reactivity makes higher acenes hardly accessible for solution chemistry, so that novel synthetic procedures are required. Here, we demonstrate the on-surface synthesis of pentadecacene (15ac), the longest acene known to date, via atom-manipulation-induced C-C-bond dissociation of a trietheno-bridged precursor on the Au(111) surface. Scanning tunneling microscopy/spectroscopy (STM/STS) and atomic force microscopy (AFM) were carried out at temperatures below 5 K to investigate the electronic properties. 15ac has an antiferromagnetic singlet (S=0) ground state characterized by a singlet-triplet gap of 124 meV and a transport gap of 1.11 eV. Spin localization and Kondo-screening was observed for Au-complexes of 15ac with an uneven number of C-Au-bonds which reveals the S=1/2 ground state of such complexes.

O 65.4 Wed 18:00 Poster C

On-surface reactions of functionalized p-terphenyl on Cu(111): kinetics of the single reaction steps involved — •Mohit Jain[1], Tamam Bohamud[1], Daniel Kohrs[2], Nathaniel Ukah[2], Hermann A. Wegner[2], and Michael Dürr[1] — [1]Institut für Angewandte Physik and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany — [2]Institut für Organische Chemie and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany

For the commonly employed coupling types in on-surface synthesis, the different intermediates formed in the course of the reactions have been investigated in great detail over the recent years. For this, the intermediates are typically induced at variable surface temperatures and are then analysed at low temperature.

In contrast to this, we study the kinetics of the on-surface reaction of 3,3"-dibromo-p-terphenyl on Cu(111) when following the reaction at constant temperature (300 K) with time. Whereas the intermediates are first dominated by long, chain-like structures, they reorganize with increasing time into small 3-membered ring structures. The process includes, a.o., breakage and formation of the involved metal-organic complexes, but trans-to-cis isomerization of the two conformers on the surface was observed to be the slowest reaction step. An almost complete phase change from a mixed phase of chain- and ring-like structures to a phase of regularly oriented, 3-membered ring structures was thus observed only on longer time scales.

O 65.5 Wed 18:00 Poster C

Theoretical investigation of dibromopyrene on sodium chloride coated copper substrate — •Florian Alexander Pfeiffer[1], André Schirmeisen[2], Daniel Ebeling[2], and Simone Sanna[1] — [1]Insitute for Theoretical Physics, Justus Liebig University Gießen, Germany — [2]Insitute for Applied Physics, Justus Liebig University Gießen, Germany

Organic 2D materials as molecular electronics are of great interest for various applications. Increasingly sophisticated methods of on-surface manipulation extend the scope of possible structure modifications to tune the electronic properties of such nanoarchitectures.

Halogenated organic precursors such as dibromopyrene (DBP) make the building blocks for assembly. A sodium chloride bilayer helps to electronically decouple the metallic surface (here Cu (111)) from the adsorbate, increasing mobility and simplifying manipulation.

Density Functional Theory (DFT) allows for bottom-up ab initio investigations of the system, while experiments reveal insights top-down, yielding mutual benefits. The DFT code of the Vienna Ab initio Simulation Package (VASP) was utilized to calculate adsorption geometry and energy with Potential Energy Surfaces (PES). Diffusion pathways and their energy barriers could be determined using the Nudged Elastic Band (NEB) method.

For further comparability with experimental results simulations of Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM), utilizing the Probe Particle Model [1], have been calculated.

[1] P. Hapala et al., Phys. Rev. B 90, 085421 (2014).

O 65.6 Wed 18:00 Poster C

Photoinduced increase of the local molecular coverage on a surface — •Christophe Nacci and Leonhard Grill — Institute of Chemistry, University of Graz, Graz, Austria

Ullmann coupling is one of the preferred reactions to synthesize covalent molecular architectures on surfaces [1]. The dissociation of specific substituents carried by the molecular precursors as well as the formation of new bonds can be triggered by different external stimuli, for instance heat, light and electric current. While the thermal control of on-surface chemical reactions is a well-established approach, only few studies report the on-surface polymerization by light.

Here, light-induced chemical reactions of an anthracene derivative on a surface [2] were investigated by combining low-temperature scanning tunneling microscopy and X-ray photoemission spectroscopy. Special emphasis is on the spatial distribution of the products, studied by position-dependent measurements. Polymerization takes place only in a limited portion of the surface, i.e., at the areas hit by the most intense laser spot. A significant increase of the local molecular coverage is observed and mainly ascribed to the local interplay between thermally induced diffusion of the adsorbed species and the reduced mobility of the grown oligomers. Moreover, despite long UV irradiations, debromination of the adsorbed species never progresses to completion within the experiment time.

[1] L. Grill and S. Hecht, Nature Chem. 12, 115 (2020) [2] C. Nacci et al., J. Phys. Chem. C 125, 22554 (2021)

O 65.7 Wed 18:00 Poster C

Electrospray Ionization Ion Beam Deposition of Organic Molecules — •Florian Münster, Lukas Heuplick, Grigori Pasko, Jan Herritsch, and J. Michael Gottfried — Department of Chemistry, University of Marburg, 35043 Marburg, Germany

When studying large molecules on surfaces, the deposition process can often be a limiting factor. While small molecules can usually be thermally evaporated using a Knudsen cell, the vapor deposition of larger molecules may be hindered by their low vapor pressure, especially if the molecules have labile functional groups. One approach to overcome these preparation-related limitations is electrospray ionization ion beam deposition (ESI-IBD). While this technique is becoming increasingly popular, for example in the preparation of large biomolecules, the precise chemical state of the deposited molecules is often unknown. For this study, we chose meso-tetraphenylporphyrin as a well-known model system to investigate the chemical state of the molecule after deposition via ESI-IBD. X-ray photoelectron spectroscopy (XPS) indicates the presence of an N-protonated species. By utilizing scanning tunneling microscopy (STM), we observed self-assembled islands composed of multiple distinguishable species, in agreement with the existence of N-protonated porphyrin molecules.

O 65.8 Wed 18:00 Poster C

Theoretical investigation of 3,3"-dibrom-p-Terphenyl on copper substrate — •Kevin Eberheim[1], Simone Sanna[1], and Michael Dürr[2] — [1]Institut for Theoretical Physics, Justus-Liebig-University Gießen, Germany — [2]Institut for Applied Physics, Justus-Liebig-University Gießen, Germany

Selectivity is a key parameter for building customized organic nanostructures via bottom-up approaches. Therefore, strategies are needed that allow connecting molecular entities at a specific stage of the assembly process in a chemoselective manner. Studying the mechanisms of such reactions is the key to apply these transformations for the buildup of organic nanostructures on surfaces. Especially, the knowledge about the precise adsorption geometry of intermediates at different stages during the reaction process and their interactions with surface atoms or adatoms is of fundamental importance, since often catalytic processes are involved. With first-principles simulations we can determine the orientation and position of the 3,3"-dibrom-p-Terphenyl as well as adsorbed mono/diradicals and the halogens. For further comparability with experimental results simulations of Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) have been calculated.

O 65.9 Wed 18:00 Poster C

Adsorption Behavior of N Heterocyclic Carbene with Thiophene on Au (111) — •Natasha Khera[1], Pranjit Das[1], Kwan Ho Au-Yeung[1], Suchetana Sarkar[1], Soyoung Park[2], Franziska Lissel[2], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany, and Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany

This research delves into the adsorption and rotation characteristics of N-Heterocyclic Carbene with Thiophene adsorbed on an Au (111) surface, employing Low Temperature Scanning Tunneling Microscopy in Ultra High Vacuum (LT-UHV STM) conditions. The molecule under investigation displays two distinct chiralities and maintains a flat/planar configuration. The molecule demonstrates rotation (chirality independent) around sulfer upon voltage pulses with the STM tip.

O 65.10 Wed 18:00 Poster C

Control of single-molecule motion on Ag(111) surface — •Donato Civita, Julia Lanz, and Leonhard Grill — Department of Physical Chemistry, University of Graz, Austria

The motion of molecules adsorbed on surfaces is fundamental for molecular collisions and reactions at surfaces, for instance in heterogeneous catalysis, on-surface polymerization or the bottom-up construction functional nanostructures. On atomically flat surfaces, the motion of adsorbed molecules can be controlled by scanning tunnelling microscopy (STM) manipulation. However, this technique was so far restricted to few nanometres of dislocation distances and limited control on the dislocation pathway. The study of single dibromo-terfluorene (DBTF) molecules on a Ag(111) surface has revealed surprisingly large distances of more than 100 nm that can be achieved with STM manipulation with picometre precision [1]. The motion of single DBTF molecules is strictly confined to one atomic row of the flat surface, rendering this system highly suitable for the study of molecular dynamics.

Here, we show that the large spatial extension of DBTF motion, and its one-dimensional confinement allow the direct measurement of the molecule traveling time with microsecond precision. Thus, we use this direct measurement to study the molecular velocity in different surface areas and in dependence of the local surroundings that appear to substantially affect the molecular dynamics.

[1] D. Civita, M. Kolmer, G. J. Simpson, A.-P. Li, S. Hecht, L. Grill, Control of long-distance motion of single molecules on a surface, Science, Vol. 370, Issue 6519, pp. 957-960 (2020).

O 65.11 Wed 18:00 Poster C

Monitoring of molecular configurations during manipulation with a scanning probe microscope — •Joshua Scheidt[1,2], Jonas Lederer[2], Hadi H. Arefi[1], Mario Infantino[1], Alexander Diener[1], F. Stefan Tautz[1], Klaus-Robert Müller[2], and Christian Wagner[1] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Jülich, Germany — [2]Fakultät IV - Elektrotechnik und Informatik, Technische Universität Berlin, Berlin, Germany

A bold vision in nanofabrication is the assembly of functional molecular structures using a scanning probe microscope (SPM). This approach requires continuous monitoring of the molecular configuration during manipulation. Until now, this has been impossible because the SPM tip cannot simultaneously act as an actuator and an imaging probe. We implement configuration monitoring using a machine learning model trained on DFT calculated data. We model the manipulation as a pre-computed Partially Observable Markov Decision Process (POMDP) in the form of a finite-state automaton, and use a particle filter to approximate the actual configuration in real time in the lab. This is enabled by a virtual reality interface in which we directly control the manipulation process and receive immediate feedback. Our proof-of-principle investigations are based on SPM manipulations of a PTCDA (3,4,9,10-perylene-tetracarboxylic dianhydride) molecule on the Au(111) surface.

O 65.12 Wed 18:00 Poster C

On-Surface Synthesis of Carbon Nanoribbons with Nonalternant Topologies — •Dong Han[1], Konstantin Y. Amsharov[2,3], and J. Michael Gottfried[1] — [1]Department of Chemistry, Philipps-Universität Marburg, Marburg, Germany — [2]Institute of Chemistry, Organic Chemistry, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — [3]Department of Chemistry and Pharmacy, Institute of Organic Chemistry II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

The graphene-based nanostructures embedded with nonhexagonal rings potentially exhibit exotic (opto-)electronic properties. However, their experimental realization remains rather challenging. Here we report the on-surface synthesis of carbon nanoribbons with several nonalternant topologies, including zigzag-shaped nanoribbon bearing 5-6-7 membered rings (dominant product) and porous nanoribbon, by lateral fusion of polyindeno[2,1-a]fluorene polymer chains on Au(111). The yield of nanoribbons is enhanced by successive molecular deposition to increase the coverage of polymer chains. The polymer chains originate from the Ullmann coupling of halogenated precursors and subsequent cyclodefluorination. The reaction species are scrutinized by scanning probe microscopy (SPM). X-ray photoelectron spectroscopy (XPS) is utilized to track the reaction process. This work demonstrates the versatility of lateral fusion in fabricating unusual carbon nanomaterials.

O 65.13 Wed 18:00 Poster C

Surface Chemical Bond and Molecular Topology of Polycyclic Aromatic Systems: Pyrene vs. Acepleiadylene — •Lukas Ruppenthal[1], Florian Münster[1], Neuhaus Leonard[1], Tim Naumann[1], Jon H. Both[1], Jan Herritsch[1], Zilin Ruan[1], Pengcai Liu[2], Xing-Yu Chen[2], Jiawen Cao[2], Jakob Schramm[3], Ralf Tonner-Zech[3], Xiao-Ye Wang[2], and J. Michael Gottfried[1] — [1]University of Marburg, Germany — [2]Nankai University, China — [3]University of Leipzig, Germany

Metal/organic interfaces have a large impact on the performance of organic (opto-)electronic devices. Therefore, the detailed understanding of their chemical, electronic and geometric structure is important for the further technological development. Many common organic semiconductors contain π-electron systems with alternant topologies, whereas non-alternant alternatives have only recently found increasing attention due to their unusual electronic properties. Here, we compare the alternant polycyclic aromatic molecule pyrene with its non-alternant isomer acepleiadylene regarding their interaction with the Cu(111) surface, using PES, NEXAFS, TPD, LT-STM, nc-AFM and DFT. We find that the non-alternant isomer shows increased metal/molecule-interaction and adsorption energy as well as a lower adsorption distance due to its reduced HOMO-LUMO gap, which brings the LUMO energetically closer to the Fermi energy of the metal, causing stronger hybridization with electronic states of the metal surface.

O 65.14 Wed 18:00 Poster C

Visualising the steps in a chemical reaction: On-surface reactivity of brominated tetraphenyl porphyrin on Cu(111) — •Ailish Gray, Michael Clarke, Matthew Edmondson, and Alex Saywell — School of Physics & Astronomy, University of Nottingham, UK

Scanning probe microscopy techniques have been extensively employed to provide details of on-surface reactions [1] and can provide significant insight into the effects of substrate and molecular chemistry upon the reaction products of on-surface synthesis.[2] The Ullmann-type coupling of brominated tetraphenyl porphyrin (BrxTPP) on Au(111) [3] is a seminal work, demonstrating molecular characterisation of on-surface covalent coupling. However, on Cu(111) the reaction progress is different,[4] and for various substrates a variety of reactions (including; ring-closing, metalorganic coordination, and self-metalation) may occur. Here, we detail a low-temperature ultra-high vacuum scanning tunnelling microscopy (STM) study of BrxTPP (x=0-4) on Cu(111). We observe multiple steps in an on-surface reaction; debromination, formation of metal-organic frameworks, ring opening, self-metalation, and covalent coupling. Systematic, temperature controlled, investigation reveals step-wise evolution of the reaction, with the intermediate reaction stages probed using STM imaging and manipulation.

[1] A. Sweetman, N.R. Champness, A. Saywell, Chem. Soc. Rev., 2020, 49, 4189 [2] L. Grill, S. Hecht, Nat. Chem. 2020, 12, 115 [3] L. Grill et.al, Nat. NanoTech., 2007, 2, 687 [4] C.M. Doyle et. al, Chem. Commun. Camb., 2011, 28, 12134

O 65.15 Wed 18:00 Poster C

On-surface degradation reactions of Pb(II)-tetraphenylporphyrin — •Cong Guo, Jan Herritsch, Lukas J. Heuplick, Stefan R. Kachel, Mark Hutter, and J. Michael Gottfried — Department of Chemistry, University of Marburg, 35043 Marburg, Germany

Metal-organic compounds of heavy main group elements are promising building blocks for the assembly of novel (opto-)electronic surface structures. However, dynamic processes of these compounds at surfaces or interfaces (i.e., chemical reactions or structural adaption upon adsorption) are largely unexplored, but can be crucial for the devices' performance. To fill this knowledge gap, we investigated the on-surface chemistry of lead(II) tetraphenylporphyrin (Pb(TPP)). On Cu(111), Pb(TPP) undergoes spontaneous transmetalation above 380 K, resulting in an exchange of the incorporated Pb ion by a Cu adatom.[1] However, a different reactivity was found for Pb(TPP) on Au(111). Here, a spontaneous demetalation of Pb(TPP) and formation of a free-base porphyrin was observed by XPS, STM, and TPD. Temperature-dependent XPS confirms the demetalation and reveals cyclodehydrogenation side-reactions of the porphyrin ligand starting above 450 K. At 720 K, re-metalation of the porphyrin with substrate Au atoms results in Au(II)-porphyrin. The observed de- and transmetalation reactions are practically relevant, because they alter the electronic and chemical properties of the metal-organic interface substantially. [1] J. Herritsch et al., Nanoscale 13, Nanoscale, 2021,13, 13241-13248 (2021).

O 65.16 Wed 18:00 Poster C

Molecular materials for carbon capture and storage: On-surface characterisation of self-assembly and thermal-stability of metal phthalocyanines — •Joseph Straw, Matthew Edmondson, Liv Warwick, James N. O'Shea, and Alex Saywell — School of Physics & Astronomy, University of Nottingham, UK

The successful capture and storage of carbon- and nitrogen-containing greenhouse gases (e.g. CO2 and NOx - produced by industrial processes) is of significant environmental importance; materials enabling gas sequestration are a route to reducing the effects of climate change. Molecular based materials, containing units which can ligate and trap gas molecules, may provide a way of selectivity and efficiency removing pollutants. Porphyrins and phthalocyanines (Pcs), both of which can be functionalised with reactive metal atoms, have been extensively studied in ultra-high vacuum (UHV) conditions.[1] Importantly, the ligation of gaseous species to the metal centres of such molecules has been shown to be feasible. [2] Here we study the formation of molecular arrays of iron phthalocyanine (FePc) on Au(111) under systematically controlled thermal conditions. We employ UHV scanning tunnelling microscopy (UHV-STM) and X-ray photoelectron spectroscopy (XPS) to characterise the morphology and chemistry of the on-surface synthesised structures and investigate thermal stability of the Pc macrocycle and extended molecular islands.

[1] J. M. Gottfried, Surf. Sci. Rep. 70, 259 (2015) [2] E. Vesselli, J. Phys. Mater. 3, 022002 (2020)

O 65.17 Wed 18:00 Poster C

On-surface synthesis of nanographenes on proximitized superconducting substrates. — •Katerina Vaxevani[1], Dongfei Wang[1], Stefano Trivini[1], Jon Ortuzar[1], and Jose Ignacio Pascual[1,2] — [1]CIC nanoGUNE-BRTA, 20018 Donostia-San Sebastian, Spain — [2]Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

Exploring molecular magnetism on superconducting substrates has the advantage over atomic spins of selectively tuning the exchange interaction with the underlying substrate. However, most elemental superconductors have highly reactive surfaces which result in the decomposition of the molecular species upon adsorption. To tackle this problem, we fabricated a metallic proximitized superconducting platform to achieve on-surface synthesis of molecular nanostructures while maintaining the superconducting properties of the substrate. First, we focused on the growth of Ag on a Nb(110) single crystal, where we find 20nm-high superconducting Ag(111) islands. There, we deposited the 2OS radical molecules to study the interaction of the molecular spin with the substrate. Additionally, we realized on-surface synthesis of the triangulene chains, previously reported only for an Au(111) pristine surface. A clear magnetic fingerprint, manifested as in-gap Yu-shiba-rusinov states, is found in some triangulene units probably because of intrinsic defects in the formation of the chains, while regular formed chains show no magnetic signal. Finally, we show our next approach for the ideal platform to study spin physics of extended pi-conjugated molecular systems.