O 29: Metal substrates 1

Time: Tuesday 10:30–12:15 Location: S052

O 29.1 Tue 10:30 S052

Controlling the translation of a single molecule — •Grant J. Simpson[1], Mats Persson[2], and Leonhard Grill[1] — [1]University of Graz, Graz, Austria — [2]University of Liverpool, Liverpool, UK

Controlling both of the orientation and the direction of translation of a single molecule is crucial to the understanding of molecular machines [1,2]. In addition, overcoming microscopic reversibility and realising unidirectional motion is a major criterion if a molecular machine is to do any meaningful work. Here, we report how single molecules can be translated in a directional manner over a metallic surface using voltage pulses from the tip of a scanning tunnelling microscope. Directionality of motion is possible due to translations occurring via an asymmetrically accessible intermediate state. The reaction pathway is discussed as well as how this molecular motion can be coupled to the motion of surface adsorbates.

[1] G. J. Simpson, V. García-López, A. D. Boese, J. Tour, L. Grill, Nat. Commun., 10, 4631 (2019) [2] G. J. Simpson, V. García-López, P. Petermeier, L. Grill, J. Tour, Nat. Nanotechnol., 12, 604 (2017)

O 29.2 Tue 10:45 S052

On-Surface Formation of Cyano-Vinylene Linked Chains by Knoevenagel Condensation — •Kwan Ho Au-Yeung[1], Tim Kühne[1], Dimitry A. Ryndyk[3,4], Gianaurelio Cuniberti[3], Thomas Heine[4], Xinliang Feng[2], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden (cfaed), TU Dresden, 01062 Dresden (Germany) — [2]Institute of Molecular Functional Materials, Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden (Germany) — [3]Institute for Materials Science, TU Dresden, 01062 Dresden (Germany) — [4]Theoretical Chemistry, TU Dresden, 01062 Dresden (Germany)

The incorporation of C=C bonds into conjugated nanostructures with additional functional groups (e.g. nitrogen substitution) has attracted extensive attention in recent years due to their intriguing electronic properties. However, the activation modes inside the toolbox of on-surface synthesis are still limited. We present the novel on-surface formation of CN-substituted phenylene vinylene chains on the Au(111) surface, thermally induced by annealing the substrate stepwise at temperatures between 220°C and 240°C. The reaction is investigated by scanning tunneling microscopy (STM) and density functional theory (DFT). Supported by the calculated reaction pathway, we assign the observed chain formation to a Knoevenagel condensation between an aldehyde and a methylene nitrile substituent.

O 29.3 Tue 11:00 S052

Self-assembly and on-surface Ullmann-type polymerisation of a DPP-based molecular wire on Au(111). — •Michael Clarke[1], Abigail Bellamy-Carter[2], Ferdinando Malagreca[3], David B. Amabilino[4], and Alexander Saywell[1] — [1]School of Physics & Astronomy, University of Nottingham, NG7 2RD — [2]School of Liberal Arts and Natural Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT — [3]School of Chemistry, University of Nottingham, NG7 2RD — [4]ICMAB-CSIC, Campus de la UAB 08193 Bellaterra Barcelona, Spain

Diketopyrrolopyrrole (DPP) is a chemical moiety which may act as an electron acceptor within organic electronic-devices and exhibits a high charge carrier mobility. [1] Charge transport within such systems is affected by the local arrangement, and orientation, of molecules/domains; hence controlled formation of ordered structures is of interest. Self-assembly of functionalised DPP species is a route towards ordered structures [2], and on-surface protocols allow monomer units to be covalently coupled under appropriate reaction conditions (e.g. Ullmann-type reactions [3]). Here we study an alkyl chain functionalised DPP unit possessing aryl-hide groups to facilitate on-surface covalent coupling. The self-assembled structure of the monomer units is characterised and ordered polymers, formed via thermal treatment, are investigated using Scanning Tunnelling Microscopy (STM). [1] Y. Li et.al, Energy Environ. Sci., 2013, 6, 1684. Y. Zang et.al, J. Am. Chem. Soc., 2018, 140, 13167. [2] A. Honda et.al , Bull. Chem. Soc. Jpn., 2015, 88, 969.[3] L. Grill & S. Hecht, Nat. Chem., 2020, 12, 115.

O 29.4 Tue 11:15 S052

Quantifying the diffusion of porphyrins on Au(111): A temperature-dependant STM study — •Matthew Edmondson and Alex Saywell — School of Physics & Astronomy, University of Nottingham, Nottingham, UK

The diffusion of surface-confined molecules is a fundamental step within the formation of self-assembled structures and on-surface reactions. Scanning probe microscopies provide a route to characterising the diffusion pathways of these molecules, and allow a quantitative analysis of energetic barriers via Arrhenius-type rate analysis.(1) In particular, SPM allows the relationship between atomic-scale surface structures and molecular diffusion to be explored; a potential method for influencing on-surface reactivity.(2)

The Au(111) surface, frequently used as a substrate for on-surface coupling reactions (3), exhibits the well-known 'herringbone' reconstruction which may influence the diffusion of molecule species. In this work, we report on the diffusion of individual 2H-TPP on the Au(111) surface; characterising the diffusion rate via variable-temperature scanning tunnelling microscopy within specific regions of the reconstructed surface. The energy barrier to diffusion (obtained via Arrhenius analysis) was found to differ between the FCC and HCP regions of the herringbone reconstruction, indicating that local geometric/electronic surface-features play a role in on-surface diffusion.

1. H. Marbach, H.-P. Steinrück, Chem. Commun. 50, 9034 (2014).
2. S. Clair, D. G. de Oteyza, Chem. Rev. 119, 4717 (2019).
3. L. Grill et al., Nat. Nanotechnol. 2, 687 (2007).

O 29.5 Tue 11:30 S052

LT-STM induced reversible chiral switching of thiophene-based molecule on Au(111) — •Suchetana Sarkar[1,2], Kwan Ho Au-Yeung[1,2], Tim Kuehne[1,2], Dmitry A. Ryndyk[2,3], Albrecht Waentig[1,4], Xinliang Feng[1,4], and Francesca Moresco[1,2] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Institute for Materials Science, TU Dresden, 01062 Dresden, Germany — [3]Theoretical Chemistry, TU Dresden, 01062 Dresden, Germany — [4]Chair of Molecular Functional Materials and Faculty of Chemistry & Food Chemistry, TU Dresden, 01062 Dresden, Germany

In the ongoing quest for miniaturization of machines, single molecule machinery holds a plethora of possibilities. Advancements in nanoscale imaging techniques, such as Scanning Tunneling Microscopy and Spectroscopy(STM, STS), allows not only the addressing of single molecules individually but through tunneling electrons/electric field stimulation with an STM tip, one can experimentally study fundamental properties of molecules such as pi-conjugation and charge transfer to a surface, and the effect it has on the switching behavior. We present the design and synthesis of a nanoswitch which exhibits a reversible switching from achiral to chiral mode on Au(111). The electronic states of both conformations have been measured with a high degree of spatial resolution, thereby showing the pathways of the electron-induced isomerization. Furthermore, we demonstrate this effect being suppressed on Ag(111).

O 29.6 Tue 11:45 S052

Enravelling effects of dispersion interactions in enantioselective adsorption — •Raymond Amador[1,2], Samuel Stolz[3], Nestor Merino-Diez[1], Oliver Groening[1], Roland Widmer[1], and Daniele Passerone[1,2] — [1]Empa - Dübendorf, Dübendorf, Switzerland — [2]ETH Zürich, Zürich, Switzerland — [3]Department of Physics, UC Berkeley, United States

van der Waals (vdW) interactions play a central role in a wide variety of systems. They are responsible for many natural processes, and thus, an accurate description of vdW forces is essential for improving our understanding physical phenomena. In this talk, we present our findings on the role of non-local vdW interactions in the enantioselective adsorption and debromination of the 10,10'-dibromo-9,9'-bianthracene (DBBA) and 9-Phenanthracenylboronic acid (9PBA) molecules, as catalyzed by chiral surfaces of the palladium-gallium (PdGa) intermetallic compound. After a brief recapitulation on the framework of density-functional theory (DFT), we discuss its principle shortcomings within the context of many-body perturbation theory, and how our current calculations address and rectify these faults via higher-order treatments of the exchange integrals. We then present several figures of interest: adsorption configurations before and after geometry optimizations and charge localization plots of adsorption, and explore effects of both vdW interactions and the nonlocal exchange term via inclusion of hybrid functionals. In doing so, we provide the foundations for further study of non-local electronic correlation in chirality.

O 29.7 Tue 12:00 S052

The role of Adatoms for the Adsorption of F4TCNQ on Au(111) — •Richard Berger, Andreas Jeindl, Lukas Hörmann, and Oliver Hofmann — TU Graz Institut für Festkörperphysik, Graz, Österreich

Molecular adsorption on inorganic substrates often includes the incorporation of native adatoms within the adsorbate layer. The presence of the adatom in the adlayer causes significant changes in the electronic structure of the interface affecting properties such as the adsorption geometry, the bonding type, and the work function. Here we investigate the adsorption of F4TCNQ on Au (111), which is a prototypical system for the adsorption of an acceptor type molecule on a metallic substrate. Using density functional theory, we show that incorporating adatoms significantly changes the interface charge transfer and modifies the Fermi-level pinning mechanism for the adsorbed species. Furthermore, we find that the 5d orbitals of the Au adatom hybridize with the F4TCNQ molecular orbitals, introducing covalent coupling within the adlayer. The combination of this effect explains why the incorporation of adatoms, despite the high cost of extracting them from the bulk, is energetically favorable.